NASA CR-151542

SEPTEMBER 1977

LMSC-D564425

THE DEVELOPMENT OF A NON-CRYOGENIC NITROGEN/OXYGEN SUPPLY SYSTEM

Prepared Under Contract NAS9-13720

by

Bioengineering Organization

LOCKHEED MISSILES & SPACE COMPANY, INC.

Sunnyvale, California

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Johnson Spacecraft Center

Houston, Texas

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List of Contributors

B. M. Greenough	Project Manager
R. E. Mahan	Project Leader
R. A. Lamparter	System Inerting Trade-off
Dr. T. Katan	Consultant

NASA Technical Monitor

R. Martin

Crew Systems Div.

NASA, Johnson Space Center

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SUMMARY

The purpose of this program was to refine the cell design, incorporate cell design improvements into the electrolysis module and test parametrically an electrolysis system capable of providing both oxygen and nitrogen. This system generates both oxygen and nitrogen from hydrazine hydrate which offers potential advantages of weight savings and less difficult resupply for long term missions, compared to high pressure gaseous or cryogenic storage.

This phase of the development of a non-cryogenic N_2/O_2 Supply System was concerned primarily with improving the system module performance through the refinement, replacement and testing of the system and some of the modular components. The major emphasis was on the cell electrodes, and the cell phase separation design. Significant mechanical and electrical performance improvements were achieved in the cathode. Improvements were also made in the phase separation area but at considerable cost in time and money and to the detriment of other investigative areas. Only the pump/bubble separator failed in a manner necessitating redesign. Its failure was, however, due to its being operated above the temperature range for which it was designed. The basic electrolysis cell design was not changed.

The approach to performance improvement involved three basic phases: 1) the selection of particular materials, processes and/or designs which promised performance improvement in the desired area, 2) the testing of the selected material/process/design in single cells and 3) full scale verification testing of the selected designs in the system module. To this

end, three separate test stations (two for single cell testing and one module testing) were assembled and used throughout the program to determine the suitability of the various components or assemblies of components under investigation.

The sections of this report that follow describe the implementation of the above approach. Process specifications are included in the appendix.

Section 1
INTRODUCTION

A nitrogen/oxygen cabin atmosphere will probably be used in future manned space missions. The nitrogen serves as an inert diluent in reducing the fire hazard in the closed environment as well as enhancing the physiological habitability of the spacecraft.

In a reclamation type life support system, the oxygen that is consumed by the crew can be recovered from metabolic wastes for recycle. Water electrolysis provides an effective process for use in this type of life support system.

Because of cabin atmosphere leakage, there is also a need for makeup oxygen and nitrogen. For short missions make up oxygen and nitrogen can be carried effectively using cryogenic or high pressure gaseous storage. However, for long duration missions, the weight penalty of these techniques becomes excessive. In using the electrolysis technique (oxygen electrolyzed from water and nitrogen catalytically decomposed from hydrazine) the oxygen and nitrogen are stored chemically as water and hydrazine in low pressure, light weight tankage. This system has the capability of automatically controlling cabin pressure and oxygen partial pressure.

The initial feasibility study of the water hydrazine electrolysis concept, the verification of the process with single cells, and the derivation of a spacecraft atmosphere control model were accomplished under Contract NAS 1-7706. Reference 1.

Contract NAS 9-10405 (Reference 2) produced a one man breadboard system which was checked out in combination with a cabin simulator. Operational data from this breadboard was used in the preliminary design of a full scale, 12 man spacecraft system. Breadboard testing in Phase II produced a data base for this technique and supported the detail design of the modular concept of a full scale system.

The major objectives of the next contract, NAS 9-13051 (Reference 3) were to fabricate one module of the modular system design and to subject it to design verification testing. These tests proved the design satisfactory with two important exceptions: 1) the cathode electrical/mechanical performance was not satisfactory and 2) the gas/electrolyte phase separator membrane proved to be incompatible with the electrolyte. While the design of the power conditioner/controller was satisfactory, further refining seemed desirable.

This contract also produced a study to determine the technology status of hydrazine vapor sensors and to evaluate techniques that might be used to measure liquid hydrazine concentration. The state of the art in vapor detectors was found to be limited to colorimetric techniques and no suitable method was found for liquid concentration measurement.

Further a mathematical model of the water/hydrazine electrolysis cell was developed for predicting heat and mass balance for a steady state condition. The model identifies key variables and defines their interrelation in the cell process. Both emperical and theoretical data were used. This model represents the first step in the development of a model capable of predicting full scale system, real duty cycle performance.

The major objectives of the program described here-in (NAS 9-13720) were to improve the electrode performance, particularly the cathode, improve the phase separation membrane performance and determine the performance of the

prototype module (including its individual components) over a range of elevated temperatures. The pump/bubble separator required some redesign and rework to accommodate the higher running temperatures.

Section 2
TECHNICAL RESULTS AND DISCUSSIONS

This section describes the tasks accomplished to improve the performance of the O_2/N_2 electrolysis module. Specific tasks were undertaken to improve the performance of the electrodes, phase separator membrane, pump/bubble separator (P/BS), and to evaluate techniques to operate nitrogen only. Also included are descriptions of testing, facilities and equipment necessary to support the individual tasks. Supporting data not included in the text are provided in the Appendix.

2.1 Electrode Development

2.1.1 Electrode Description and Development Objectives

The electrodes of the O_2/N_2 prototype module use a mixture of platinum (Pt) black and iridium (Ir) black as the catalyst. The mixture, which includes a "binder" and an "extender", is impressed into a nickle (Ni) screen which is welded on to a Ni support rim. The rim provides the electrical connections for the electrode as well as "O" ring sealing surfaces. The "binder" material literally binds the mixture together. The "extender" takes up space initially, and so when leached out provides porosity in the electrode. These electrodes are used in a circulating electrolyte type of cell. See Figure 1.

Preparation and application of the catalyst mixture are the most important aspects of electrode fabrication and as such have presented the most problems. There are three basic and interrelated areas of concern; 1) finding constituent formulation ratios which provide optimum electrical performance while, 2) maintaining a completely homogeneous and repeatable mixture which, 3) adheres well to the support screen. Further, once the catalyst

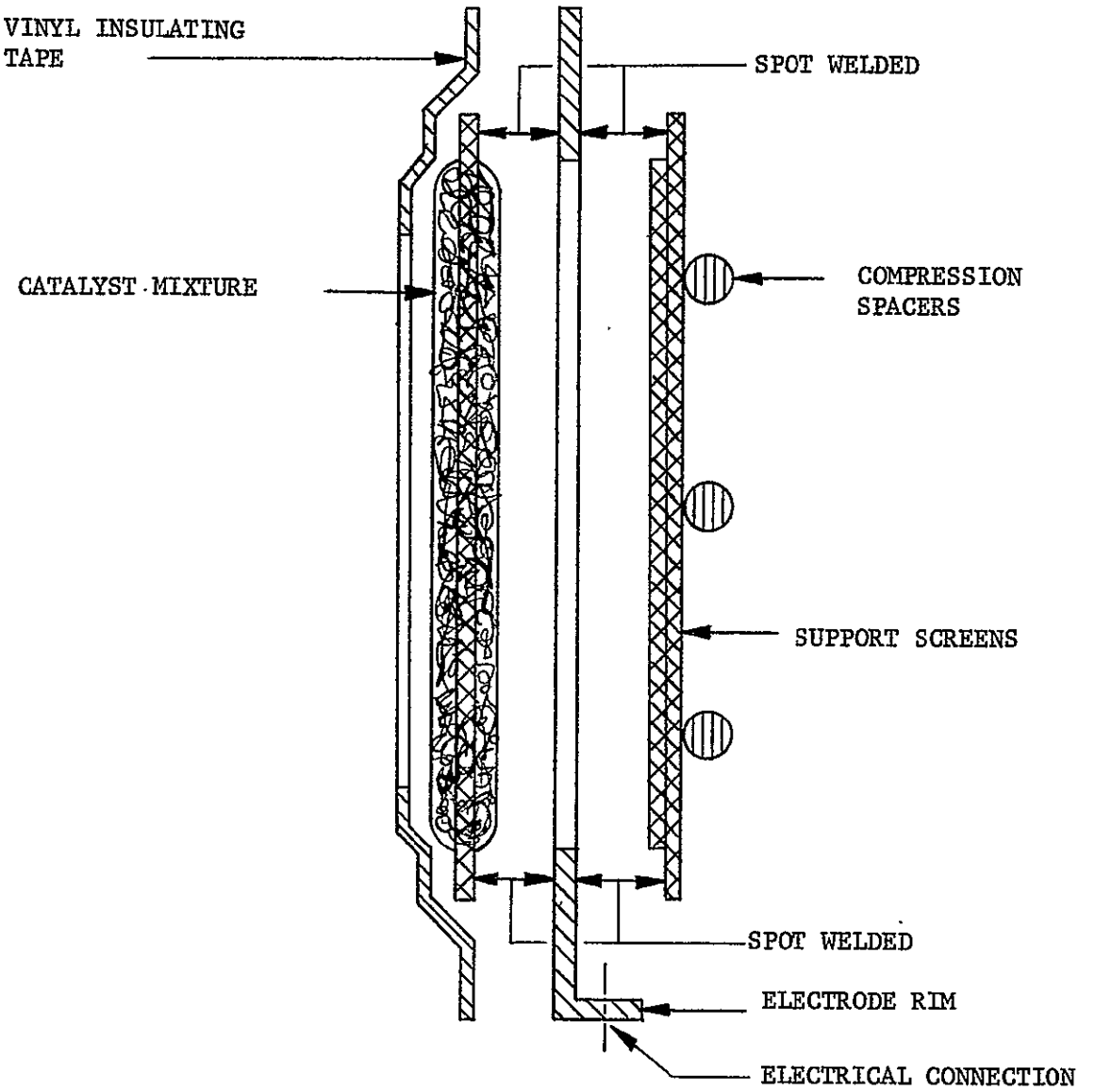


Figure 1 Electrode Configuration

mixture is applied to the support screen, it must be able to withstand the rigors of a leaching process. This process removes most of the extender material, leaving the mixture very porous (a requirement) and rather fragile (not a requirement). This fragility can be reduced somewhat by increasing the amount of binder (a suspension of teflon particles in toluene) in the mixture. However, the binder has the undesirable effect of encapsulating the catalyst particles with teflon, which insulates them electrically from both the electrolyte and the support screen. This results in higher internal resistance and shows up as increased voltage for a given current density.

2.1.2 Electrode Formulation Investigation

2.1.2.1 Small Scale Electrode Test Setup and Procedure

The electrode formulation investigation was begun by fabricating a test set-up (Figure 2) which would allow the rapid testing of a large number of small electrode samples. The set-up included the following components:

1) A laboratory, electrolytic "H" cell capable of accommodating an anode or a cathode sample.
2) A potentiostat which provided variable and controlled current to the cell as well as the corresponding voltage readout (or vice versa).
3) A motor potentiometer to provide variable current or voltage sweep rates from the potentiostat.
4) An X-Y plotter which recorded current vs voltage during the current/voltage sweeps.
5) Gaseous hydrogen supply for the reference electrode.

In order to duplicate, as nearly as possible, the conditions within the prototype cell, the electrode samples were tested in two different ways. First, the sample was immersed completely in the electrolyte. This accomplished two things, it thoroughly wetted the sample and simulated a flooded electrode. Once an emersed voltage/current sweep was recorded, the sample was removed and reinserted such that only one side was in contact with the electrolyte. The sample was held and positioned by a micrometer controlled vertical slide which allowed precise and repeatable positioning of each sample. This simulated a normal, non-flooded electrode and once again a voltage/current sweep was made and recorded.

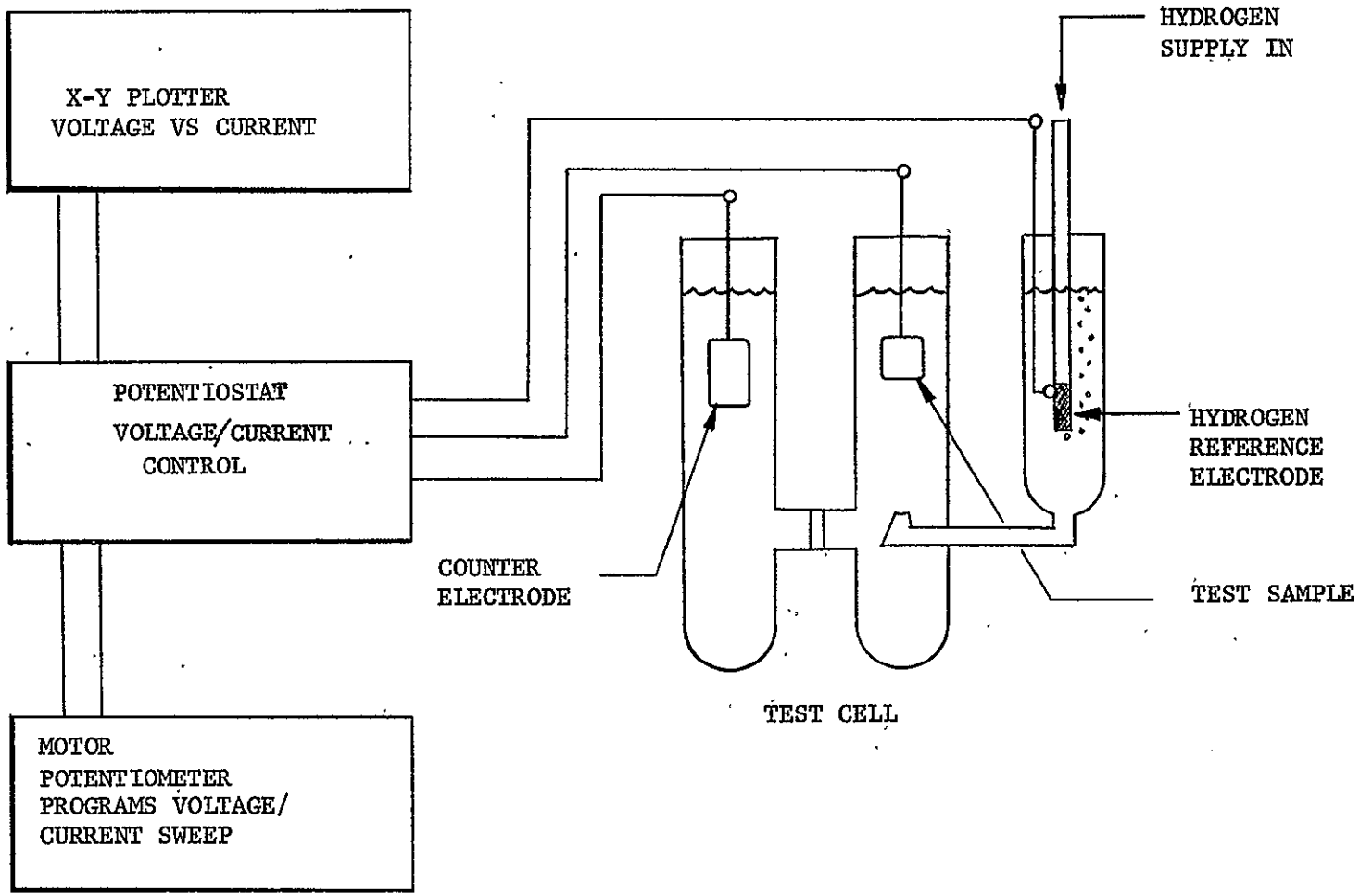


Figure 2 Test Set-Up, Small Scale Electrodes

2.1.2.2 Small Scale Anode

Candidate formulations and matrices were made for test screening in which a range of weight ratios were used of the four anode constituents previously used in the engineering prototype module developed under contract NAS 9-13051. See Table 1. The catalyst area for each full scale electrode is 145 cm^2 (22.5 in^2).

Sample No.	Variable	Substrate	Platinum Black ~ grams	Iridium Black ~ grams	Binder, Aqueous Teflon ~ grams	Extender, "Jaguar"*~ grams
1		Ni Screen	2.11	0.11	2.22	2.97
2		Ni Screen	2.638	0.132	2.22	2.97
3**		Ni Screen	1.58	0.079	2.22	2.97
4**		Ni Screen	2.11	0.0825	2.22	2.97
5**		Ni Screen	2.11	0.11	2.775	2.97
6		Ni Screen	2.11	0.11	1.665	2.97
7**		Ni Screen	2.11	0.11	2.22	3.7125
8		Ni Screen	2.11	0.11	2.22	2.2275

Table I Initial Formulation Matrix Anode

The baseline anode (Sample No. 1) utilized ratios identical to those of the prototype module anodes. The range of weight of individual constituents tested was approximately ±25% of the baseline quantities. Since previous data indicated that the optimum amount of Iridium was between the prototype anode amount (5% of the Platinum used) and no Iridium, three quantities of it, different from the baseline were tested rather than two.

*Jaguar is a tradename of a substance used commercially as a food extender, but the precise formulation is not available.

**Note in Figure 3 that these samples did not reach the desired consistence or gel condition.

Samples 1 through 8 and 24 and 24A were made using aged extender (Jaguar)* while 22, 22A, 23 and 23A used fresh extender. The performance of all tested anode samples is summarized in Figure 3. A typical current/voltage sweep is shown in Figure 4. Supporting data plots are shown in the Appendix.

To obtain each test sample, an anode approximately 2 in. (5.1 cm) x 2 in. (5.1 cm) was made. Each anode was subjected to the standard leaching procedure (Reference 3) and then had one or more 1 cm^2 (.16 in^2) samples cut from it for testing. Where more than one sample was taken from a given anode, the second sample is denoted by the letter A.

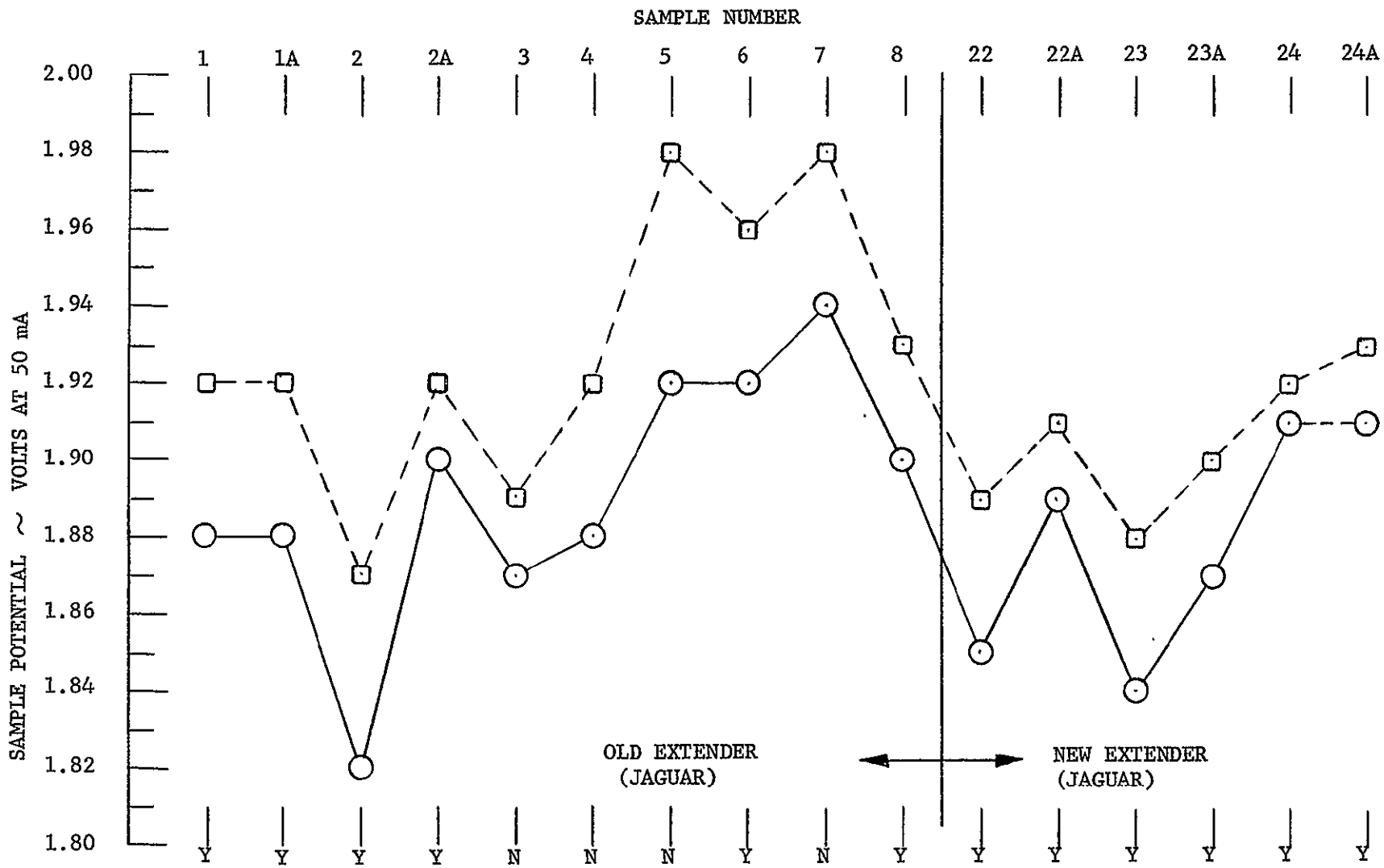
2.1.2.3 Small Scale Anode Test Results and Discussion

Upon completing the testing of samples 1 through 8, a second sample (1A) was cut from a different area of the #1 anode. Its electrical performance was identical to the original #1 sample (see Figure 3 plus 1 and 2 Appendix).

Sample 2 showed the lowest potential of any sample tested. However, sample 2A (cut from the same anode) did not repeat that performance (Figure 3). The implication is that the catalyst mixture was not spread evenly across the anode. Approximately one week after the testing of anode 2, anode 24 was made to the same formulation, (as anode 2), using the same aged extender. This was to determine if the improved performance of anode 2 could be repeated. It was not. Samples 24 and 24A repeated each other and 2A but resembled the baseline data (sample 1) rather than sample 2 (Figure 4 and Appendix Figures 3, 14 and 15). This tends to define sample 2 as a random success.

The initial conclusion drawn from the small scale anode testing was that future anodes be formulated as samples 22 and 23, being certain to always use fresh extender. This conclusion was based on the somewhat lower

*Jaguar is a tradename of a substance used commercially as a food extender, but the precise formulation is not available.



ANODE SCREENING TEST SUMMARY

Figure 3

ELECTRODE SCREENING, VOLTAGE/CURRENT PROFILE
SAMPLE #1 (BASELINE)
ELECTRODE/ELECTROLYTE CONTACT:
SAMPLE AREA: 1 CM²
SWEEP RATE: 30 V/HR
13 JUNE 1974
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

FIG. 4

voltage profiles of samples 22 and 23. However, it was later learned that the mixture did not always adhere well to the support screen. This was attributed to the fact that mixtures 22 and 23 are dry mixtures, the extender (Jaguar) having been reduced by 25% (Figure 3). Since the voltage reduction of samples 22 and 23 over the baseline anode and conclude that no significant performance improvement (mechanical and electrical) could be made by varying the baseline anode formulation.

2.1.2.4 Small Scale Cathode

The amount of Pt catalyst in the cathode mixture is a compromise. On one hand, relatively large quantities of Pt are necessary to produce the low, internal (cell) electrical resistance which provides low cell power requirements. On the other hand, smaller amounts of Pt are required to minimize the amount of hydrazine decomposed at the cathode. Previous attempts to minimize Pt content in the cathode resulted in a significant reduction in the volume of the catalyst mixture. The reduced volume was inadequate to completely cover the 22.5 in^2 (145 cm^2) cathode window. Also the mixture, when spread, was so thin and fragile that large quantities would sluff off during the leach procedure. It became obvious that the solution was to find another material which could at least be substituted for the Pt removed and perhaps even be used to increase the total volume of the catalyst mixture.

A brief investigation resulted in acetylene carbon black being chosen as the Pt black substitute. Both weight and volume substitutions were made. As expected, weight substitution proved unsatisfactory because the carbon black is considerably less dense than the Pt. black. It was also shown that a given volume of carbon black required more of the liquid components (binder and extender) than did the same volume of Pt black. An initial group of about 20 different catalyst mixtures were made to define some rough boundaries for the component ratios. Only six were suitable for application to screens and only two were acceptable, from a mechanical standpoint, once they were applied to the screens. Table I shows the mixture

formulation for the five samples which where tested for electrical performance. The small scale cathodes were tested in the same manner as the small scale anodes previously described including voltage/current sweeps with the sample both immersed and in surface contact only.

SAMPLE MAKE UP	GRAMS	1C111	5C	10C	13C	14C
Platinum		1.32	0.88	0.44	-0-	-0-
Carbon		0.22	0.44	0.99	1.50	1.50
Teflon		2.13	2.34	3.73	5.90	6.49
"Jaguar"		2.10	2.31	4.97	7.87	8.66

Table II Cathode Catalyst Sample Formulation

2.1.2.5 Small Scale Cathode Test Results and Discussion

No particular performance improvement (over prototype module cathode) was noted for any sample although sample 1C111 (high Pt/C ratio) was comparable to the cathodes of the prototype module. Table III shows voltages required at each of three current densities.

	VOLTS REQUIRED FOR:					
	200 mA/cm^2		150mA/cm^2		130 mA/cm^2	
	SAMPLE-ELECTROLYTE CONTACT		SAMPLE-ELECTROLYTE CONTACT		SAMPLE-ELECTROLYTE CONTACT	
SAMPLE NO.	SURFACE ONLY	SUBMERGED	SURFACE ONLY	SUBMERGED	SURFACE ONLY	SUBMERGED
1C111	0.84	0.73	0.66	0.56	0.58	0.50
5C	0.90	0.84	0.75	0.70	0.70	0.64
10C	0.93	0.86	0.79	0.74	0.74	0.69
13C	0.96	0.93	0.82	0.80	0.77	0.74
14C	0.94	0.87	0.80	0.75	0.74	0.70

Table III Cathode Voltage - Current Profile

Another series of small scale cathodes was made in which the amount of Pt used was reduced to 75%, 50%, 25%, 15%, 10% and 5% of the standard Pt

loading, 78 m gm/in^2 (12 m gm/cm^2). The Pt so deleted was replaced with an equal volume of carbon black. The 5% mixture was not tested as it would not adhere to the support screen. As shown in Figure 5, the standard Pt loading can be reduced by 50-70% with little change in electrical performance. All of the above samples were made using "on-hand" binder (teflon). New binder was purchased and some additional samples were made to see if any performance differences would appear between electrodes using, new and old binder. The new binder electrodes showed only minor improvement in electrical performance but showed significant improvement in mixture workability and adhesion characteristics. New binder and extender was used in all succeeding electrodes produced.

During the course of the cathode formulation investigation, Dr. T. Katan of Lockheed's R&D facility (Palo Alto, Ca.) suggested an alternate source of electrode material. One square foot of this material was purchased from Energy Research Corp (ERC). The material was tested as a small scale cathode. Its electrical performance (Figure 16 Appendix) was almost identical to the Lockheed 25% Pt, 75% carbon cathode. This performance is interesting in that the Lockheed material provides the same performance as the purchased material but uses only about 1/3 the Pt. The ERC material has a Pt coverage of 10 mg/cm^2 while the Lockheed material has coverage of only 3.2 mg/cm^2.

The small scale cathode investigation resulted in the selection of the cathode mixture formulation shown in Table IV, where it is compared to the prototype module (Std) cathode formulation.

	QUANTITY/CATHODE ~ GM	
COMPONENT	PROTO. MOD. STD CATHODE	"NEW" CATHODE
Pt	1.76	0.464
C	-0-	0.199
Binder (Teflon)	1.85	1.943
Extender (Jaguar)	2.47	2.594

Table IV Cathode Mixture Formulation

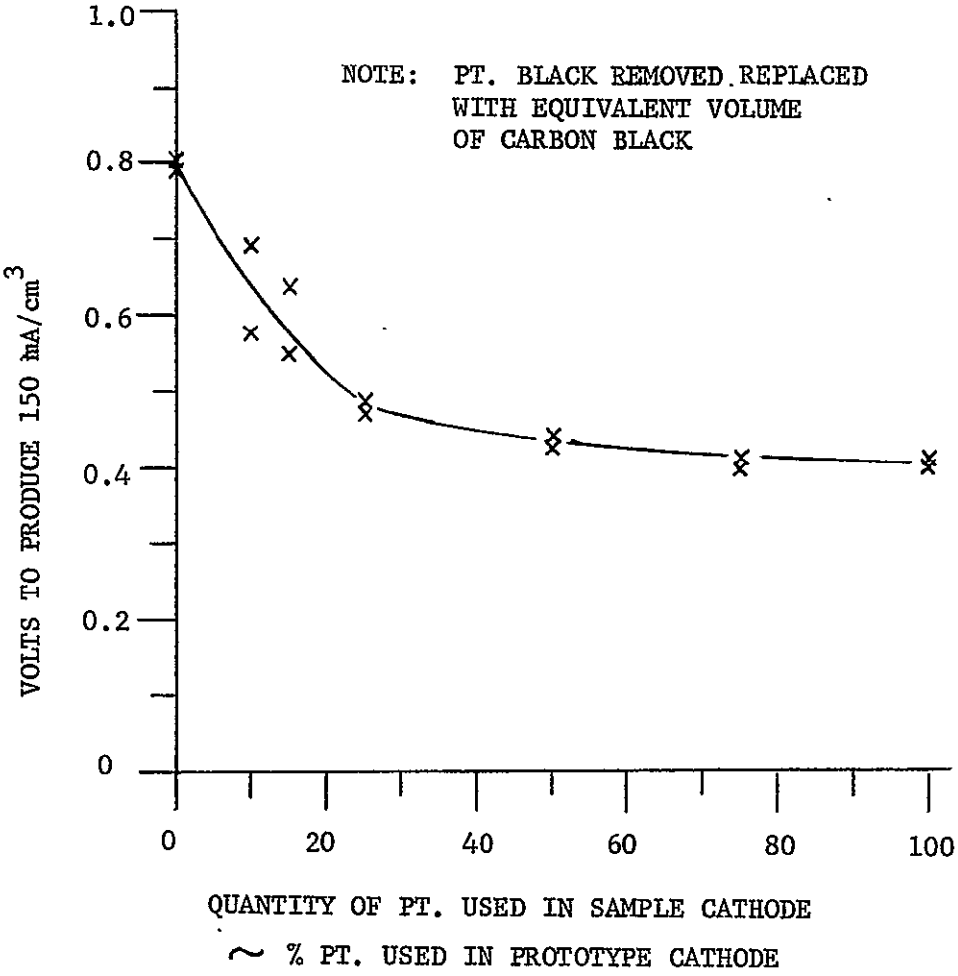


Figure 5 Electrical Performance of Pt. Black/Carbon Black Cathodes

The "new" formulation is the result of reducing the Pt of the standard formulation by 75% and replacing it with carbon black. The standard amounts of binder and extender were retained. One final change was made to the "new" formulation: the quantity per electrode was increased by increasing the weight of each component by 5%. The increased size allowed more reliable application to the support screens. Table IV indicates the "new" constituent weights including the 5% increase.

2.1.2.6 Full Scale Electrode Fabrication & Test

The full scale electrodes were fabricated as they were for the prototype module using the catalyst formulations selected from the small scale electrode task. In the case of the anode, the formulation is identical to that used in the prototype module. Catalyst compositions for both electrodes are shown in Table V.

	QUANTITY PER ELECTRODE ~ GMS	
COMPONENT	ANODE	CATHODE
Platinum (Blk)	6.32	0.464
Iridium (Blk)	0.33	-0-
Carbon (Blk)	-0-	0.199
Binder (Teflon)	6.65	1.943
Extender (Jaguar)	8.90	2.594

Table V Electrode Catalyst Formulations

Both formulations are also dependent on batch size with respect to workability and physical properties. Therefore cathode batches are sized for 2 cathodes. Once the 2 unit cathode mix has been worked to the proper "chewing gum" consistency, it is cut and weighed into 2, equal, single cathode batches. Anode batches are large enough to be mixed one at a time.

The electrode mixture is applied to the support screen in a somewhat different manner than was used on the prototype module electrodes. Instead of being worked through the screen from one side only, each (single) electrode batch is divided and each half is rolled into a square "pancake" the size of the electrode window. One "pancake" is applied to each side of the support screen and the assembly is rolled, thus embedding the support screen within the catalyst mixture. For a detailed description of the catalyst mixture application see Design Standards and Process Specification in the Appendix.

Once the catalyst mixture has been applied and dried each assembly must be leached. The leaching procedure is designed to do four things to the electrode: 1) remove any residual toluene (the suspension medium for the teflon binder) and oil, 2) remove the extender (Jaguar) so that the mixture will be porous, 3) remove any impurities which may be present, and 4) sinter the teflon into the porous, structural mass which binds the catalyst particles together and to the support screen. The leaching is shown in Table V, below.

Solution	Duration ~ Min	Ultrasonic Bath	
		Yes	No
Propanol	15	x	
H_2O, distilled	15	x	
30% KOH, boiling	120		x
H_2O distilled	15	x	
10% H_2SO_4	15	x	
H_2O, distilled	15		x
30% KOH	720		x
H_2O distilled	60		x

Table VI Electrode Leaching Procedure

The testing of the full scale electrodes was done in conjunction with the cell development and hydrazine tests and is documented in Section 2.2 following.

2.2 Cell Development

This section includes the testing of the full scale electrodes as well as the buildup and test of the full scale single cells. It further includes a discussion of the interrelated problems encountered with the phase separation membrane and gassing in the electrolyte upon the addition of hydrazine.

2.2.1 Full Scale Electrode Testing

The full scale electrode testing was done with two, full scale single cells and under a variety of conditions. This section discusses first the electrode long term performance with KOH only, and with no change in test conditions or hardware, once the test was started. Thus, the initial test data is baseline. Electrode performance data was also obtained under different conditions including elevated temperature, hydrazine, and various membrane materials. The results of these tests are also discussed in this section.

The long term electrode/cell test with KOH only ran for a total of 4800 hours (200 days). During this time, the cell experienced 5 automatic shut downs. The first shut down occurred at about 1180 hours, and was caused by a low reservoir condition which resulted from no water feed for about 30 hours (over a week-end). During this time the KOH concentration steadily increased, eventually reaching a maximum of 41%. No performance degradation was noted as a result of the high concentration. The cell was restarted after sufficient water was added to bring the electrolyte to a normal concentration of 30%. All voltages returned to their pre-shut-down values within one hour of restart. This indicates that the electrodes and cell can tolerate significant variations in electrolyte concentration with no ill effects. The remaining four shut downs were due to power failures and were short in duration and of no consequence.

In order to provide a direct comparison between the power requirements of the new electrodes and the electrodes in the prototype module, the long term cell was run at a current density of 129 mA/cm^2 (18.75 A total).

After the initial start up, it took the anode and cathode approximately 20 hours to reach their stable running voltages of 1.63 and 0.33 volts respectively. Total cell voltages was 1.96 volts. This represents a small improvement in cell voltage over the prototype module value of 2.1 volts. Figure 6 shows a typical 460 hour period, while the figures of Appendix H show the voltage history for the entire 4800 hours.

The second type of variation noted was the long term, gradual rise in cell voltage. This increase was largely due to the cathode as the anode voltage stayed essentially constant (for a given current density). The rate of increase was very low, averaging 1.75 mV per week (0.01 mV/hour). While this is of little consequence in itself, it should be considered in conjunction with other factors which tend to increase electrode power requirements; e.g. the addition of hydrazine.

A possible explanation for this increase is suggested by the fact the electrolyte loop is not closed for single cell testing. The reservoir is open to the air. CO_2 from the air combines with the KOH forming potassium carbonate (K_2CO_3). Past testing indicates that K_2CO_3 (which is less soluble in water than KOH) in the electrolyte tends to degrade electrode performance, particularly in the case of the cathode. The effect is exaggerated if the gas over electrolyte differential pressure (ΔP) is allowed to increase so that the electrode runs drier than normal. Some of the K_2CO_3 crystalizes on the electrode, reducing effective catalyst area and degrading electrical performance. Even though the ΔP may be reduced to reestablish normal electrode wetness, the K_2CO_3 does not readily dissolve and continues to degrade electrode performance.

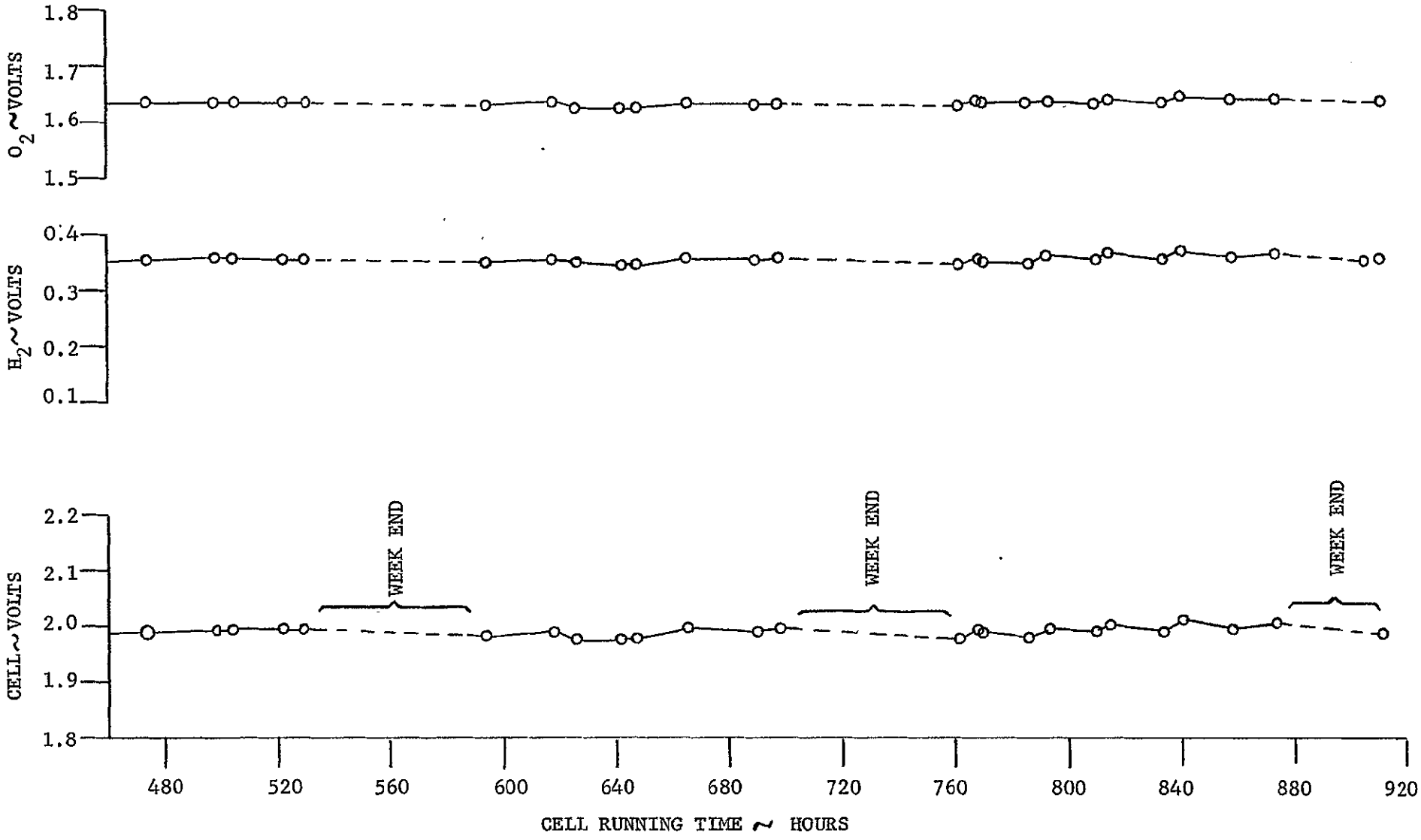


Figure 6 Long Term Single Cell ~ Typical Time History

At 2100 hours into the long term cell test, a series of varying current density runs was initiated. The purpose was to provide the current density/voltage profiles of the electrodes. Table VII (below) lists the set current, current density, the associated cell anode and cathode voltage and each run's duration. Figure 7 shows the current/voltage profile for the cell and both electrodes. The average lab temperature during the runs was 70.9°F with a standard deviation, (σ) of 1.5°F. With

Run #	Current Density mA/cm^2	Current Amps	Average Voltage Volts Cell	Anode	Cathode	Duration Hours
1	69	10	1.809	1.574	0.235	6
2	83	12	1.805	1.589	0.261	18
3	97	14	1.913	1.608	0.305	6
4	110	16	1.946	1.619	0.327	16
5	138	20	2.055	1.660	0.395	18
6	150*	21.75	2.110	1.679	0.431	4
7	166	24	2.132	1.687	0.445	18
8	179	26	2.185	1.710	0.475	24
9	193	28	2.224	1.723	0.501	26
10	200	29	2.259	1.730	0.529	24

*Max Design Current Density
**Data Figs. 21, 22 Appendix

Table VII** Current Density/Voltage Profiles
Long Term Single Cell

the lowσ the tests can be considered to be comparable. Subsequent experience with the single cell indicates that a lab ambient temperature of about 70-71°F yields a running electrolyte temperature of about 80-85°F. A full cell stack (22 cells) running at max design current (21.75A) and using the long term cell electrodes would require 46.5 volts. This is about 3.5 volts above the original design goal of 43 volts.

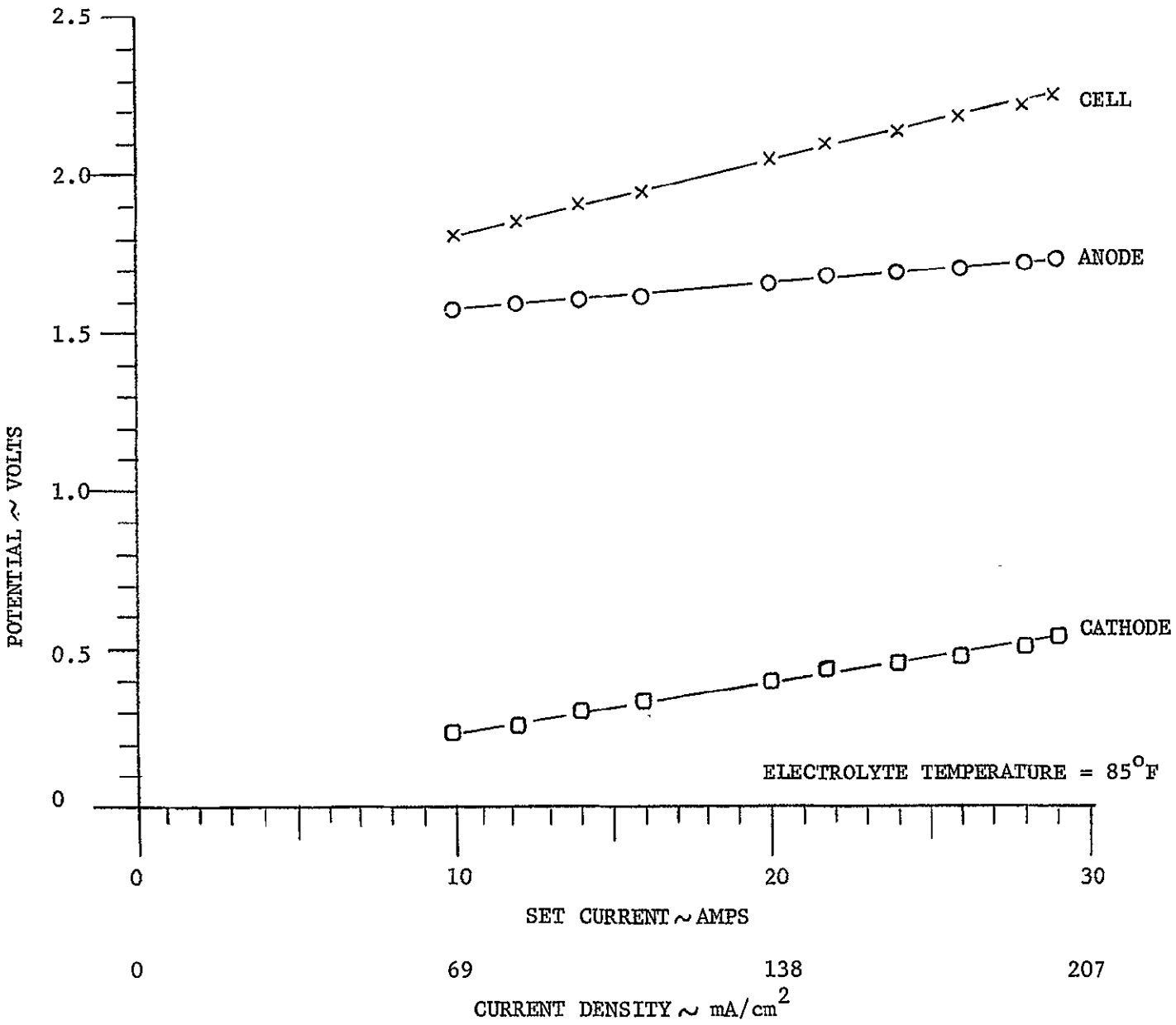


Figure 7 Current Density vs Cell Anode and Cathode Potential

2.2.2 Phase Separator Membrane/Hydrazine Investigation

After successfully running the prototype module (fabricated under Contract NAS 9-13051) for approximately 500 hours, on KOH only, gas appeared in the electrolyte. Examination revealed that it was coming from the cell stack and gas analysis showed it to be predominately, but not totally hydrogen. The cell stack was disassembled and a sufficient number of electrolyte spacers were leak checked to show that 13 out of 24 Acropor membranes were leaking gas even though wet. Further, two membranes had small, visable holes (no membrane material within the reinforcing weave). Close inspection of the interfacing support screens showed nothing to indicate mechanical puncture. The Acropor membrane is intended to be the primary gas barrier in the cell keeping the evolved gas, which is back pressured, separate from the liquid electrolyte.

The vendor, Gelman Instrument, was contacted and informed of the problem. He relied that the Acropor membrane was chemically incompatible with KOH above 3 molar (the electrolite is approximately 7 molar) and with hydrazine in any concentration. This was contrary to the information received from the vendor when Acropor was selected, again under Contract NAS 9-13051. A search was immediately started to find a replacement for the Acropor.

Six candidate membranes were selected for compatibility and performance testing:

1. Quartz with cellulose backing - Pallflex Products.

   This was intuitively unacceptable although the vendor thought it compatible.

2. Asbestos with neoprene binder - Pallflex Products
3. Teflon with polyethylene backing - Millipor.

   This was basically hydrophobic but vendor claimed it could be made hydrophilic by treatment withwetting agent. KOH appeared to wet it.

4. PVC - Millipor
5. PVC - Stokes Div., Electric Storage Battery (EBS)
6. Fine Mesh Nickel - Buckbee Mears.

The compatibility soak eliminated numbers 1 and 4 after about 5 days. The quartz membrane simply started dissolving while the Millipor PVC turned brown (was originally white). Millipor informed us that the discoloration indicated that the KOH was reacting with the PVC. The remaining samples survived the soak test. The Stokes PVC was the first material to be tested in a single cell. It performed its phase separation function but produced a 0.3-0.35 volt cell voltage increase over the "non membrane" baseline configuration. The increase occurred primarily at the anode. Later, the PVC membranes leaked gas through pin holes which had gone unnoticed during their installation in the electrolyte spacer. Stokes indicated that the holes were due to the lack of quality control (Q.C.). The PVC's primary use was as battery separators and as such only minimal Q.C. was required; i.e. pin holes were acceptable. The PVC was therefore dropped at this point as a candidate membrane.

The initial membrane screening led to the selection of the fine mesh (10 um) nickel by Buckbee Mears. This material's primary draw back was its price: $12,000 for a full cell stack, which works out to about $350/cell. In spite of its high cost, it was decided to order 2 ft^2 and test it in full scale cells. It's advantages lay in the facts that 1) it was known to be chemically compatible with both KOH and N_2H_4 and 2) the membrane had its own integral reinforcing structure which would allow two (2) support screens to be removed from behind each membrane.

Single cell testing with the nickel membrane and hydrazine showed excessive gassing in the electrolyte. As a preliminary test, a single 15 cc charge of 64% hydrazine was added to a single cell. At that point, that particular cell had accumulated 1238 hours running on 30% KOH only. Small amounts of gassing were observed in the electrolyte but were considered insignificant. A voltage increase of 0.05 volts was noted. The test was terminated, the cell refilled with fresh KOH and restarted. At 1258 hours a second 15 cc hydrazine charge was added to the same cell. Gassing was less

than produced by the previous charge but the voltage rise was greater, showing 0.18 volts by 1264 hours. By 1300 hours the voltage had reached 2.8 volts for an increase of 0.3 volts. At 1400 hours the cell voltage had decayed to about 2.57 volts and a 2 molar charge of hydrazine was added to the cell. By 1406 hours the voltage had reached 2.87 volts and the electrolyte in the reservoir was completely opaque with gas. During the course of the test oxygen production dropped from 100% to 68% while nitrogen rose from 0 to 32%. No other gasses were detectable at the anode. The test was terminated.

Since it was not readily apparent where the hydrazine was breaking down, it was decided to make a run with a small injection of hydrazine and with the heat exchanger removed. This produced the same results as the previous runs with hydrazine even though a second small charge was added after the first charge. It was concluded that while the heat exchanger was trapping gas, it was not causing decomposition of the hydrazine. A second 2 molar charge was added to the system without the heat exchanger. The test was allowed to run for two hours by which time the voltage had risen 0.2 volts. Again there was considerable gassing in the electrolyte, though less than previously. It was concluded that some of the hydrazine was decomposing on the surface of the Buckbee Mears membrane and that the gas formed was causing the voltage increases by blocking electrolyte contact with the electrode. Beaker tests were made which showed that gassing did occur when the BMC material was placed in a solution of 30% KOH + 2 molar hydrazine. This served to substantiate the conclusion that hydrazine decomposition was occurring at the BMC membrane.

Two solutions to the problem presented themselves: replace the BMC membrane with a material which would not provide decomposition sites or act catalytically, or, coat the BMC membrane with some material which would isolate it from the electrolyte and would not itself act as a catalyst or provide decomposition sites. As potential fixes were discussed, it became obvious that <u>both</u> the replacement and coating approaches should be pursued.

The search was initiated with a literature survey concerned primarily with identifying suitable coatings for nickel. At the same time several vendors were contacted for suitable membranes of materials other than nickel. Also Olin Chemical Co. (a producer of Hydrazine) was contacted to determine what materials are in contact with hydrazine during its manufacture. Only 304 stainless steel is used (which tended to verify the conclusions reached with respect to the heat exchanger.) It was therefore decided to test as many forms of stainless steel membranes as could be acquired. Stainless samples were provided by Michigan Dynamics and Union Carbide and were of three different forms: 1) woven wire cloth, 2) matted wire fibers, 3) porous sintered sheet.

Dr. T. Katan of LMSC's Palo Alto research facility was consulted as to potential coatings for the BMC membrane. He suggested eight different coatings and prepared eleven samples for beaker testing. He also ran bubble point tests on all of the samples. The results of the sample testing (including stainless steel and other materials) are summarized in Table VIII. Two additional samples were to be run as soon as they were received. One was a stainless steel woven wire cloth whose nominal pore size is 5 micron (μm), the other was a sulfuric acid based passivation treatment for nickel. The procedure for the passivation treatment later proved unsatisfactory for our purposes and was never used.

In the meantime and in order to acquire additional baseline data, a 90 cm^2 single cell was assembled using parts from a cell stack which had operated successfully on 2 molar hydrazine. This cell contained no phase separator membrane other than Acco asbestos and was in all respects identical to past successful 90 cm^2 cells. After the cell voltage had stabilized on KOH/H_2O only, a 2 molar charge of hydrazine was added. Within approximately two minutes, gas began to appear in the electrolyte. The rate of gas production stabilized at about 50 cc/hr. The test was terminated and a KTA type analysis was performed to determine what, if any, differences existed between this test and previous hydrazine tests with

Table VIII

Test Results

Sample #	Description & Vendor	Base Mat'l	Treatment	Surface	Immediate Gassing?	Gassing After Several Hours?	Gassing After Several Days?	Bubble Point cm H_2O (psi)	Potentially Useful	Comment
I	BMC 10μm seive	nickel	400°C, .5 hr in air	Perf. grainy blue	No	No	Some	115(1.64) 119(1.69)	No	Color gone after several days.
II			300°C .5 hr in air	Perf. grainy gold brown	No	No	Some		No	
III			Clean in alcohol H_2O rinse	Perf. grainy grey	No	Some	Some		No	As used in 2 single cells much gassing
IV	Johnson & Johnson cotton gauze	cellu-lose + seizing	None	-	No	No	No	N.A.	Maybe	Showed no apparent deterioration after approx. 400 hr. soak
V	Johnson & Johnson Cotton balls	cellu-lose								
	From 90 cm^2 electrode frame	nickel	gold plate	solid, bright	Yes	Much	Much	-	No	Verifies Olin comments
K1	BMC 10μm sieve	nickel	2 hrs in H_2 atm at 400°C	Perf. grainy	No	Very little	Very little	115(1.64) 119(1.69)	Maybe	Gassing at edges mostly
K2			Phosphate I	Discarded because of increased pore size (2-3 times)						
K3			Phosphate II	Discarded because of increased pore size (1.5-2 times)						

Table VIII (continued)

Sample placed in 30% KOH/2 molar H_2H_4)

Sample #	Description & Vendor	Base Mat'l	Treatment	Surface	Immediate Gassing	Gassing After Several Hours?	Gassing After Several Days?	Bubble Point cm H_2O (psi)	Potentially Useful	Comment
K4			Phosphate/ chromate	Perf. grainy grey blue	No	Some	Some	115(1.64) 119(1.69)	No	Long Edge
K5	BMC 10μm seive	nickel	Chrom. Electro-plate 1 min.	Perf. grainy grey blue	No	Much long edge only	Little	115(1.64) 119*1.69)	Maybe	
K6			Chrom. Electro-plate 2 min.		No	Much all over	Very little (long edge)		Maybe	
K7			Chrom. Electro-plate 4 min.		Very little	Much all over	Very little (long edge)		Maybe	
K8			Thiourea Treatment		Much	Much	Small Amt (long edge)		No	
K9			Parafin in Benzene		Much	Much	Much		No	
K10			7M KOH anodic 4 min 50 A/cm^2	Same as untreat-ed	Little	Much	Little		No	
K11			7M KOH cathodic 4 min 50 A/cm^2		Little	Much	Very little		No	

Table VIII (continued)

Sample placed in 30% KOH/2 molar N_2H

Sample #	Description & Vendor	Base Mat'l	Treatment	Surface	Immediate Gassing	Gassing After Several Hours?	Gassing After Several Days?	Bubble Point cm H_2O (psi)	Potentially Useful	Comment
K9	Clevite sintered nickel	Nickel	None	Very grainy grey	Much	Much	Much	90.7(1.29) 96.7(1.38)	No	
10	Union Carbide sentered S.S.	S.S.	None	Very grainy light grey	None	Very little	Very little	56.9(.81) 71.7(1.02)	No, (B.P.)	
12	Michigan Dynamics Dutch twill	304 S.S.	None	Porous Bright	None or very little	None or very little	None or very little	59.5 (.85) 87.0(1.24)	No, (B.P.)	
13	Mich. Dynamics mat.	304 S.S.	None	Porous textured grey	Some	Much	Much	40.4(.57) 47.0(.67)	No,(B.P.)	Had visable holes in it.
14	Mich. Dynamics Dutch twill	304 S.S.	Heated to gold color in air	Porous, bright gold	Little	Some	None or very little	59.5(.85) 87.0(1.24)	No,(B.P.)	Gold color disappeared after about 8 hours
15	Michigan Dynamics	304 S.S.	Heated to blue color in air	Porous textured blue	Some	Much	Much	40.4(.57) 47.0(.67)	No,(B.P.)	Blue color disappeared after about 6 hours.

90 cm^2 cells which had little or no gassing. This analysis showed the only significant difference to be the brand of hydrazine used. The original hydrazine tests run in 90 cm^2 cells used Eastman 64% practical grade hydrazine. In anticipation of increased hydrazine usage, Baker 64% practical grade had been substituted since it was more readily available and some what less expensive.

In order to determine whether or not different brands of hydrazine did behave differently, several brands and grades were purchased and tested. The first test used MCB, 97% (in H_2O) hydrazine in the above mentioned 90 cm^2 cell. Gassing amounted to about 2.3 cc/hr, a reduction in gassing by a factor of about 20. This encouraged the subsequent testing of the following brands and grades of hydrazine in the 90 cm^2 cell.

1. MCB, 99-100% hydrazine
2. Mallenchrodt, 99% organic reagent grade hydrazine
3. Eastman, 64% (in H_2O), practical grade hydrazine

The amount of gas produced in the electrolyte by the MCB 99-100% and the Mallenchrodt 98% hydrazine was about the same as with the MCB 97% hydrazine; 2.3-2.5 cc/hr. However, the Eastman 64% particle hydrazine produced gas at a rate of 15 cc or 5-6 times the others. The Eastman hydrazine was next run in a 145 cm^2 cell which had the newly acquired 304 ss screen installed in place of the BMC material. While some gas did appear in the electrolyte the amount was so small that it was not measurable. Although little or no gassing occurred, a sharp increase in cell voltage was noted. Initial cell voltage was 2.15 volts. Within two hours of the hydrazine addition, it had risen to 2.69 volts. The cell was allowed to run and after 115 hours the voltage had dropped only to 2.35 volts. At this point a second 2 molar change was added to see if the first test could be repeated. Again, the maximum voltage was 2.65 volts with no measurable gas in the electrolyte.

As a result of the foregoing, it was decided to proceed as follows:

1) If the 5 micron (μm), stainless steel, woven wire cloth had a bubble point at least equal to the BMC nickel membrane, it (the stainless steel) would be subjected to full scale, long term testing in conjunction with hydrazine and if successful, incorporated in the module design.
2) If 1) provides unsatisfactory, hydrogen fired and/or chromium plated BMC membranes would be subjected to the same testing.
3) If neither 1) or 2) was successful, an attempt would be made to locate a suitably configured membrane of pure cellulose to be tested in as 1).

The 5 micron (μm) stainless steel membrane as subjected to bubble point and loading tests in a 145 cm^2 cell and did indeed prove equal to the BMC nickel membrane. It was subsequently incorporated into the cell assembly.

2.2.3 Hydrazine Efficiency Tests

The single cell used for this test had been operated for approximately 160 hours on KOH/H_2O only prior to the hydrazine run. Cell voltage had stabilized at about 2.0 volts. All three voltages (cell, anode and cathode) were very close to their counterparts in the long term cell. A gas chromatograph was attached directly to the anode side ΔP regulator to minimize gas analysis error due to sample contamination. The test was initiated with the addition of a nominal 2 molar charge of hydrazine to the electrolyte loop. An electrolyte titration shortly thereafter showed the actual hydrazine molarity to be 2.4. The hydrazine addition brought the usual voltage increase of about 0.09 volts and considerable amounts of gas were noted in the electrolyte. At least part of this gas was due to exposed nickel in the heat exchanger. Figure 8 shows Nitrogen/Oxygen buildup and decay, hydrazine concentration decay and cell voltages.

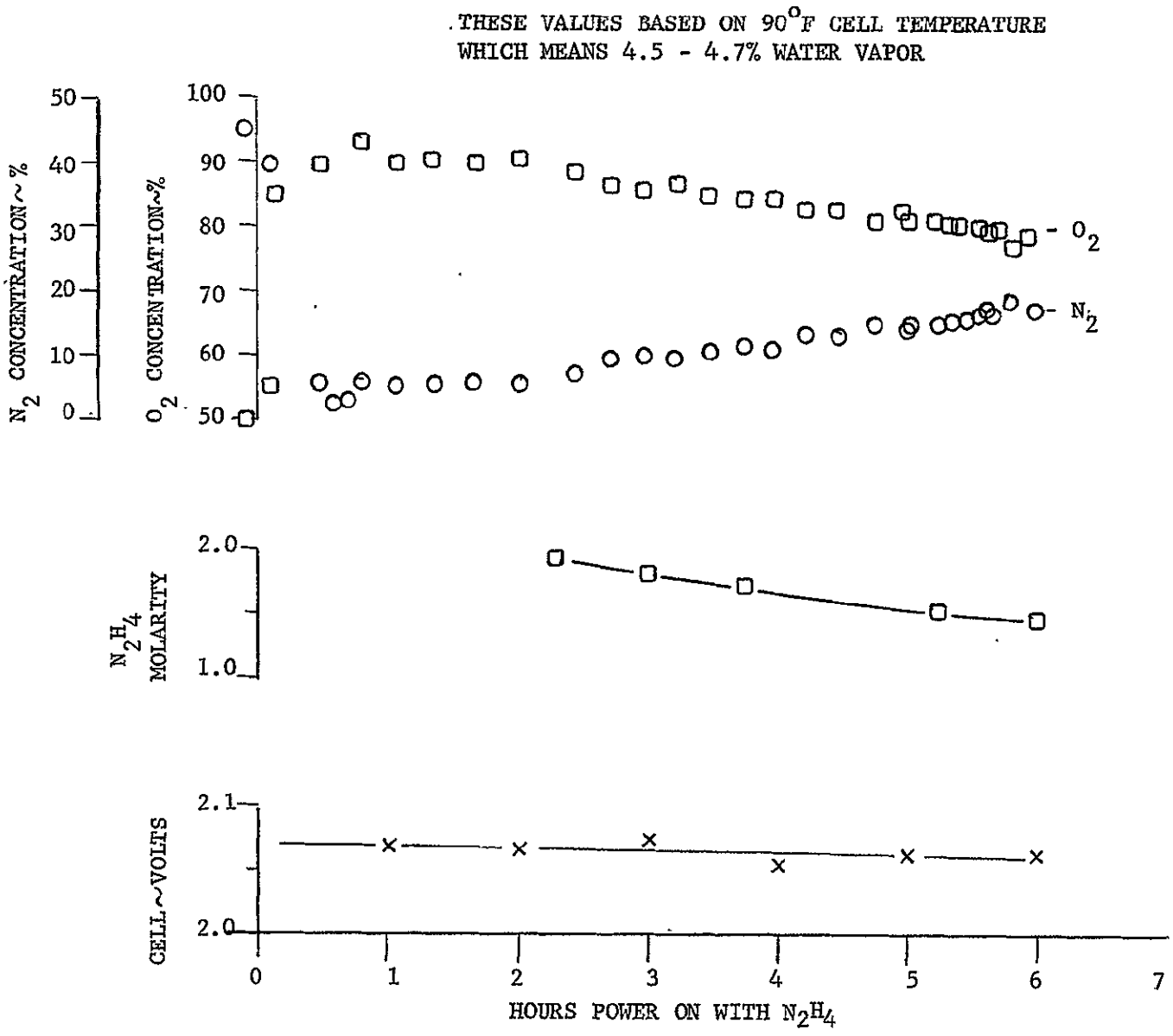

THESE VALUES BASED ON 90°F CELL TEMPERATURE
WHICH MEANS 4.5 - 4.7% WATER VAPOR
N_2 CONCENTRATION~%
50
40
30
20
10
0
O_2 CONCENTRATION~%
100
90
80
70
60
50
O_2
N_2
N_2H_4 MOLARITY
2.0
1.0
CELL~VOLTS
2.1
2.0
0
1
2
3
4
5
6
7
HOURS POWER ON WITH N_2H_4

Figure 8

Hydrazine efficiency calculations (anode) were made using two different approaches. The first method used cathode gas flow, anode gas flow and anode gas analysis. Cathode gas flow prior to the hydrazine addition is compared to cathode gas flow after hydrazine addition. Any increase in flow rate represents nitrogen production at the cathode and the value can be calculated from the change in flow rate. Anode gas flow rate is measured and anode gas analysis defines that fraction which was nitrogen. Anode hydrazine efficiency is then defined as:

$$\frac{\text{Anode } N_2 \text{ Production Rate}}{\text{Anode } N_2 \text{ production rate} + \text{Cathode } N_2 \text{ production rate}}$$

This method showed an anode mean efficiency of 82.5% with a standard deviation of 3.5%.

The second method compares anode nitrogen production, from gas flow and analysis as above, to "available" nitrogen production. "Available" nitrogen production is calculated using hydrazine concentration data, i.e. titration data. This method showed anode mean efficiency to be 85.5% with a 0.6% standard deviation. The two methods verify each other within data tolerances and anode efficiency is considered to be between 80% and 85% and quite satisfactory.

2.2.4 Single Cell Elevated Temperature Tests

Single cell elevated temperature tests were completed with promising results. Nine runs were made with electrolyte control temperatures ranging from 70°F (21°C) to 109.4°F (43°C). The individual thermobulbs used for temperature control were calibrated at the following values: 70(21), 75(24), 85(29), 91.6(33), 96.8(36), 100(38), and 109.4°F (43°C). Data was taken at the same time in each cooling cycle to insure that a given series of data points would represent the same electrode temperatures. Voltage repeatability for a given control temperature was excellent

indicating a consistent electrode vs. control temperature correlation. The electrode (anode and cathode) operating temperature is somewhat higher than the control temperature. The Δt is unknown since the control temperature is measured external to the cell and the cell construction precludes internal temperature measurements. Figure 9 presents plots of control temperature vs cell, cathode and anode voltages. It is interesting to note that the inverse effect of temperature on cathode voltage is somewhat reduced as the control temperature increases while the opposite is true with respect to the anode. The effects of temperature are also discussed in Sections 2.3.2.1 and 2.4.4.1.

2.3 Electrolysis System Buildup, Checkout and Test

2.3.1 Component Fabrication and Rework

2.3.1.1 Cell Spacers

Since this module was to be used for the system parametric and 90 day tests, it was necessary to decide whether to: 1) have new spacers molded or 2) rework the existing electrolyte spacers to accept the stainless steel membrane and use the old gas spacers. Cost was a significant factor, and option 2) would have cost about $500 and would have provided only one complete cell stack and no spacers. On the other hand option 1) provided two (2) complete cell stacks plus spares with a minimum order and for a total cost of $350. Option 1) was chosen.

Since a large number of spare spacers were available, it was decided to use some of them, in destructive tests, to investigate the cause of spacer warping previously encountered during the annealing process. It was suspected that vertical temperature gradients across the interior of the annealing oven were largely responsible for spacer warping. It was further suspected that the rate at which the spacers were brought to annealing temperature effected the amount of warpage. Therefore a series of tests were performed to determine whether or not the spacer annealing procedure could be improved. The results of these tests showed the following;

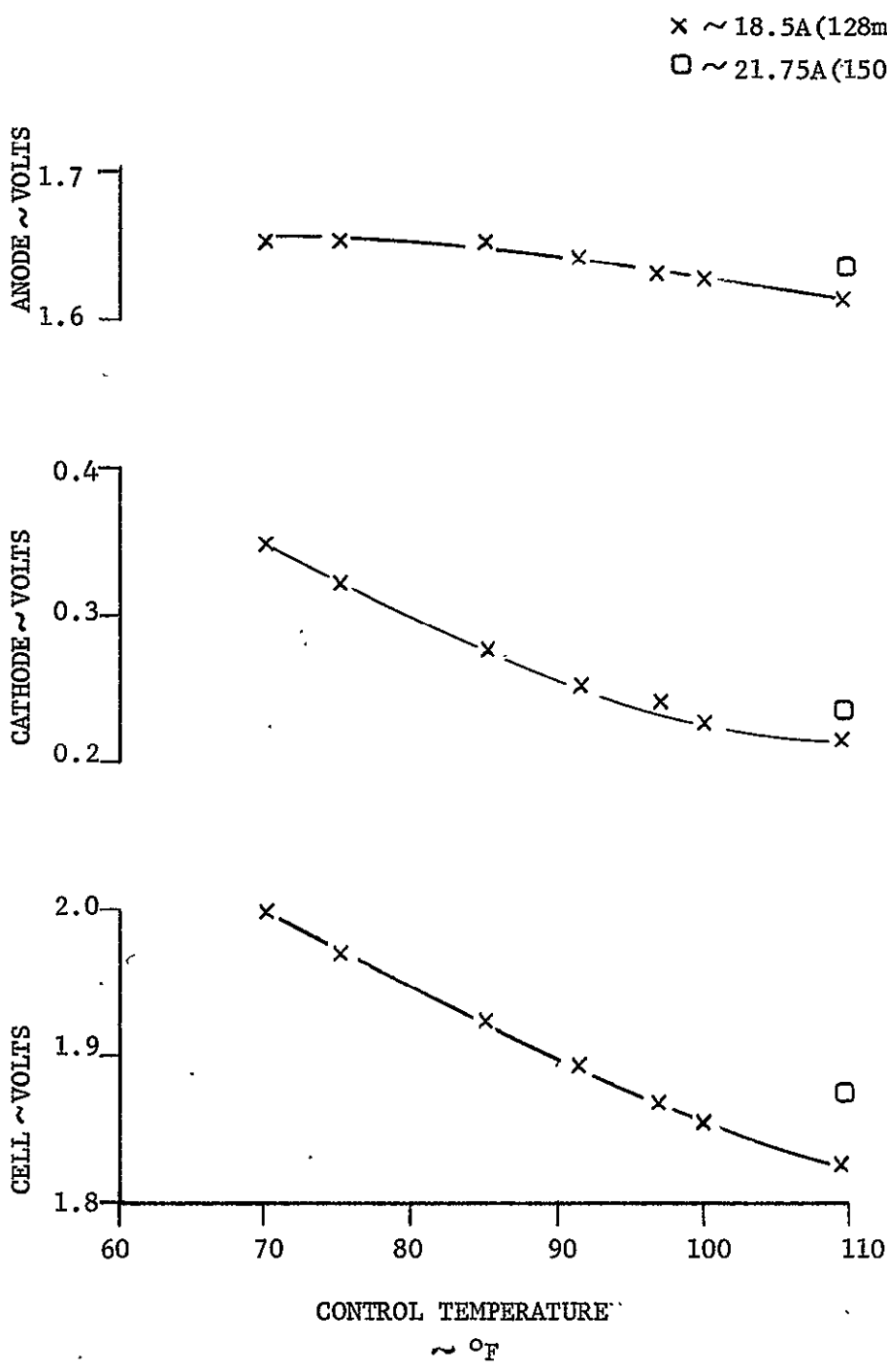


Figure 9 . Cell, Cathode and Anode Voltage
vs Control Temperature

1) the original time, temperature, relationship provided by Union Carbide (330°F (166°C) for 3.5 hours) were optimum. 2) Temperature rise rates up to about 30°F (17°C) per minute were acceptable. 3) Temperature gradients across the part of 5°F (3°C) or less produced little or no warpage of the part. All remaining spacers were annealed with no warpage. Figure 10 shows the time temperature annealing curve as a function of part thickness.

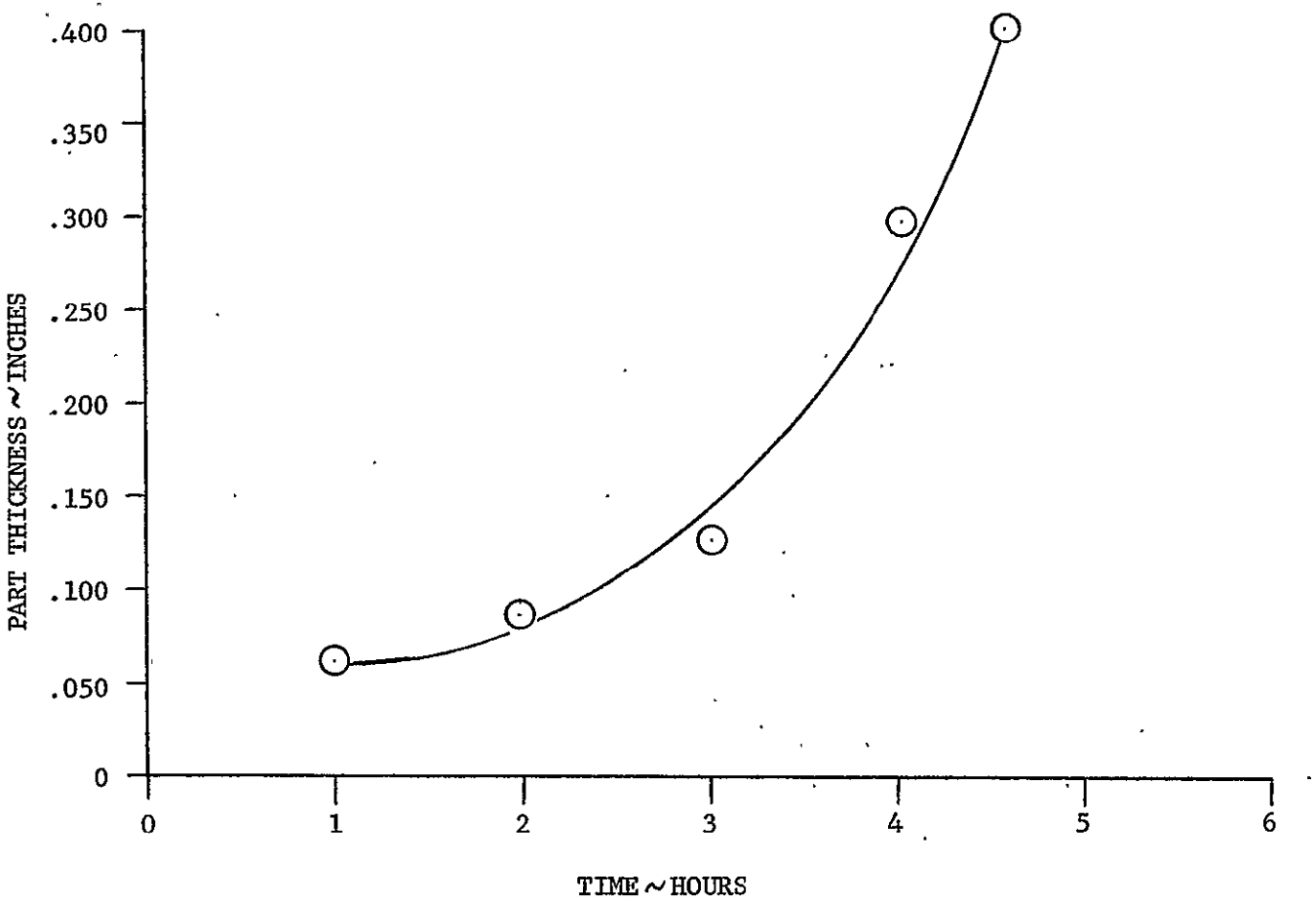
2.3.1.2 Electrodes

A complete set of 44 electrodes was fabricated with only one problem being encountered during the process; one cathode had to be remade because large quantities of catalyst mixture sluffed off the screen during the leaching procedure. The problem was traced to improper weighing of the carbon black and a second batch was prepared and successfully applied to the screen.

The electrodes were fabricated according to the formulations and leaching procedure shown in Section 2.1.2.6. Although each electrode is fabricated separately and by hand, the process has become fairly rapid and results in a high degree of performance repeatability from electrode to electrode. The time required to learn to fabricate these electrodes would probably be relatively short.

2.3.1.3 Baseplate

Since the module baseplate had been fabricated for and used during the preceeding contract, NAS 9-13051, it was subjected to a thorough inspection prior to its incorporation into the "new" prototype module. All fluid and gas passages were pressure tested to 10 psi while at room temperature and at approximately 150°F (66°C). The elevated temperature test was accomplished by placing the pressurized base plate in a container of water and then raising the water temperature to about 150°F (66°C). No leaks, cracks or delaminations were found and the baseplate was judged suitable for use in the "new" prototype module.



AIR ANNEALING PART THICKNESS VS. TIME AT 330°F

Figure 10

One minor modification was made to the baseplate in order that a thermobulb could be placed in the cell stack electrolyte outline. This was for electrolyte temperature control and required only the enlarging of an existing hole.

2.3.1.4 "New" Prototype Module Assembly

The first step in the module assembly was to install the new cell stack. Previous cell stack assembly was very tedious because the large "O" rings were very difficult to retain in the grooves in the electrolyte spacers long enough to complete the stack up of all the cells. It was therefore decided to tack all the large "O" rings into their grooves with spots of rubber cement, which had been shown to be compatible (when dry) with the electrolyte. Once this was done, the assembly of the stack was actually rather easy and was accomplished on the first try.

All the remaining module components (reservoir, pump/bubble separator (P/BS) and solenoid valves), were disassembled, cleaned and leak checked prior to installation in the module. The reservoir was found to have a leaking Bellofram which was replaced.

2.3.1.5 Test Station Buildup

The test station, for the module system parametric and 90 day tests, was installed in a pressure vessel and is shown in schematic form (along with the complete test set-up) in Figure 11. A gas analyzer is shown installed in line with the two gas outputs of the cell stack. This analyzer was never used as it proved to be erratic and unreliable. Gas was instead sampled with a syringe and septum.

2.3.2 Module, Test Station and Component Checkout

System check out was performed using water as the electrolyte and no power to the cell stack. The first of two check out runs was made at room temperature and produced no anomolies anywhere in the system. The second run was made with the electrolyte temperature at 130°F (54°C) which caused a failure in the P/BS. System checkout was completed with no further problems.

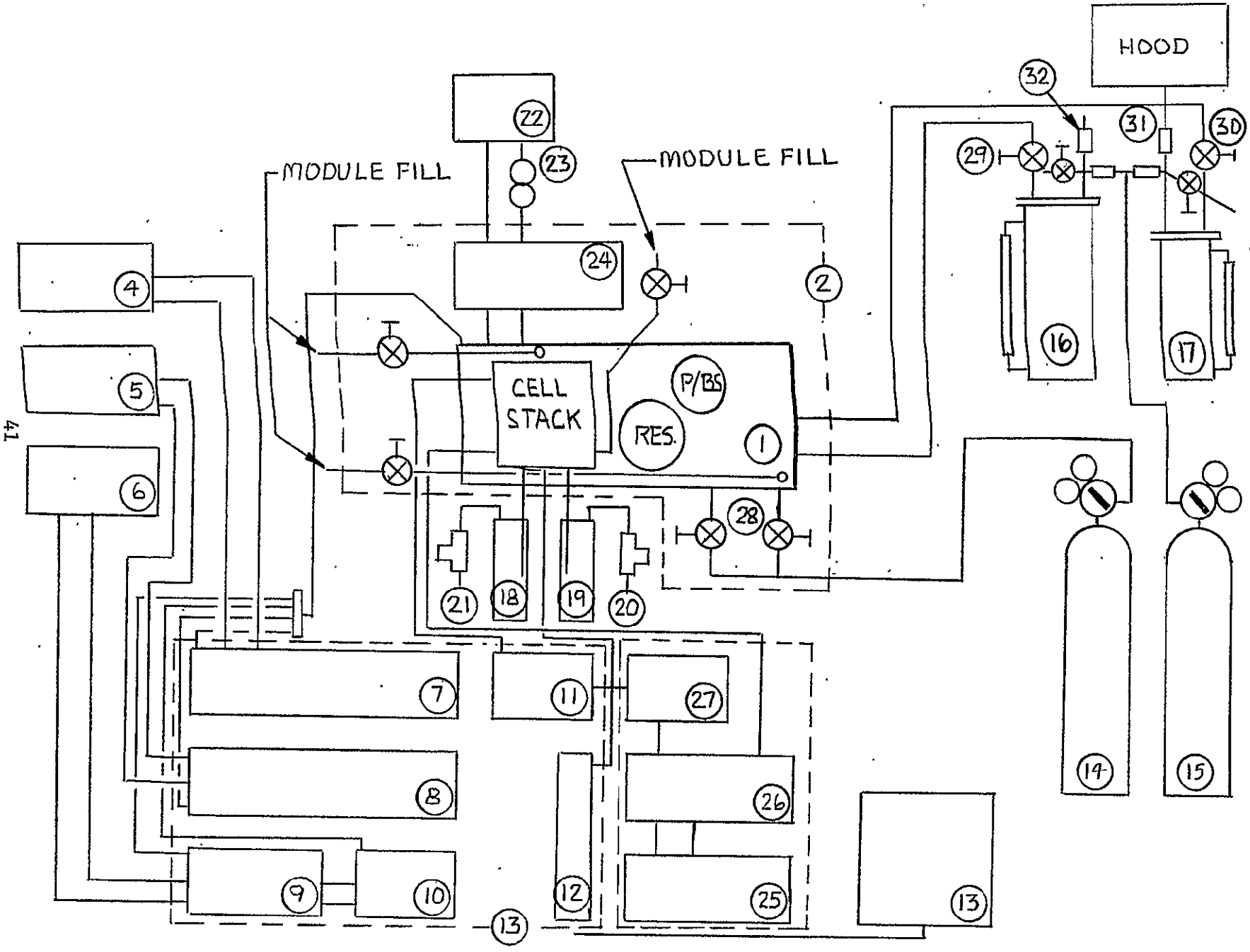


Figure 11 Schematic, O_2/N_2 Test Facility

Item	Description
1	Prototype Module
2	Pressure Vessel
3	Primary Control Panel
4	Power Supply, Reservoir
5	Power Supply, Pump/Bubble Separator
6	Power Supply, Primary Panel
7	Reservoir Set and Control
8	Pump/Bubble Separator Control
9	System Status
10	Feed Control
11	Ammeter, Cell Stack Current
12	Connector Panel, Cell Stack Read-out
13	Data Logger
14	N_2 Supply, Purge
15	N_2 Supply, Feed Tank Pressurization
16	Feed Tank, Water
17	Feed Tank, Hydrazine
18	Bubbler, O_2/N_2
19	Bubbler, H_2
20	Sample Port, H_2
21	Sample Port O_2/N_2
22	Water Heater
23	Pump
24	Heat Exchanger
25	Power Supply Cell Stack
26	Hi/Lo Mode Timer/Switch
27	Strip Chart Recorder, Current
28	Shut-Off Valves, N_2 Purge
29	Shut-Off Valve, Water Feed
30	Shut-Off Valve, Hydrazine Feed
31	Safety Valve, Hydrazine Tank
32	Safety Valve, Water Tank

Figure 11A Component List for O_2/N_2 Test Schematic

2.3.2.1 Pump/Bubble Separator Operation

During the checkout run made with the electrolyte temperature at 130°F (54°C), the P/BS began making unusual noises which were assumed to be bearing noises. Soon after the noises began, the unit failed to dump gas which was being injected into the electrolyte. (Gas is injected into the electrolyte as part of the P/BS checkout procedure). The system was shutdown and the P/BS removed and disassembled.

Inspection showed that the bearings were O.K. and that the noises were caused by the impeller face rubbing the end face of the interior cup. The failure of the unit to remove gas was the result of scrapings from the impeller face plugging the gas outlet orifice.

The overall failure was due to the loss of axial clearance between the impeller and the interior cup of the unit. The large difference in thermal coefficient of expansion (TCE) between the polysulfone interior cup and the outer stainless shell cuased the loss of clearance at higher temperatures. The TCE of polysulfone is 2.7 times that of stainless steel. The cross section sketch of Figure 12 shows where the interference occurred.

An attempted fix was made by machining the impeller and interior cup faces to provide an additional .014 inches of clearance at room temperature. This clearance was calculated to provide adequate clearance up to about 165°F (74°C). Tests verified the clearance up to about 160°F (70°C). The excessive clearance at room temperature reduced pumping efficiency making electrolyte circulation startup very difficult at lower temperatures.

After the P/BS was repaired, it was reinstalled in the module and operated to circulate KOH over a week-end at room temperature. In preparation for continuing the system parametric tests and during the rise in the system temperature, the P/BS began making noises similar to those heard previously. The system was shut down and the P/BS again disassembled.

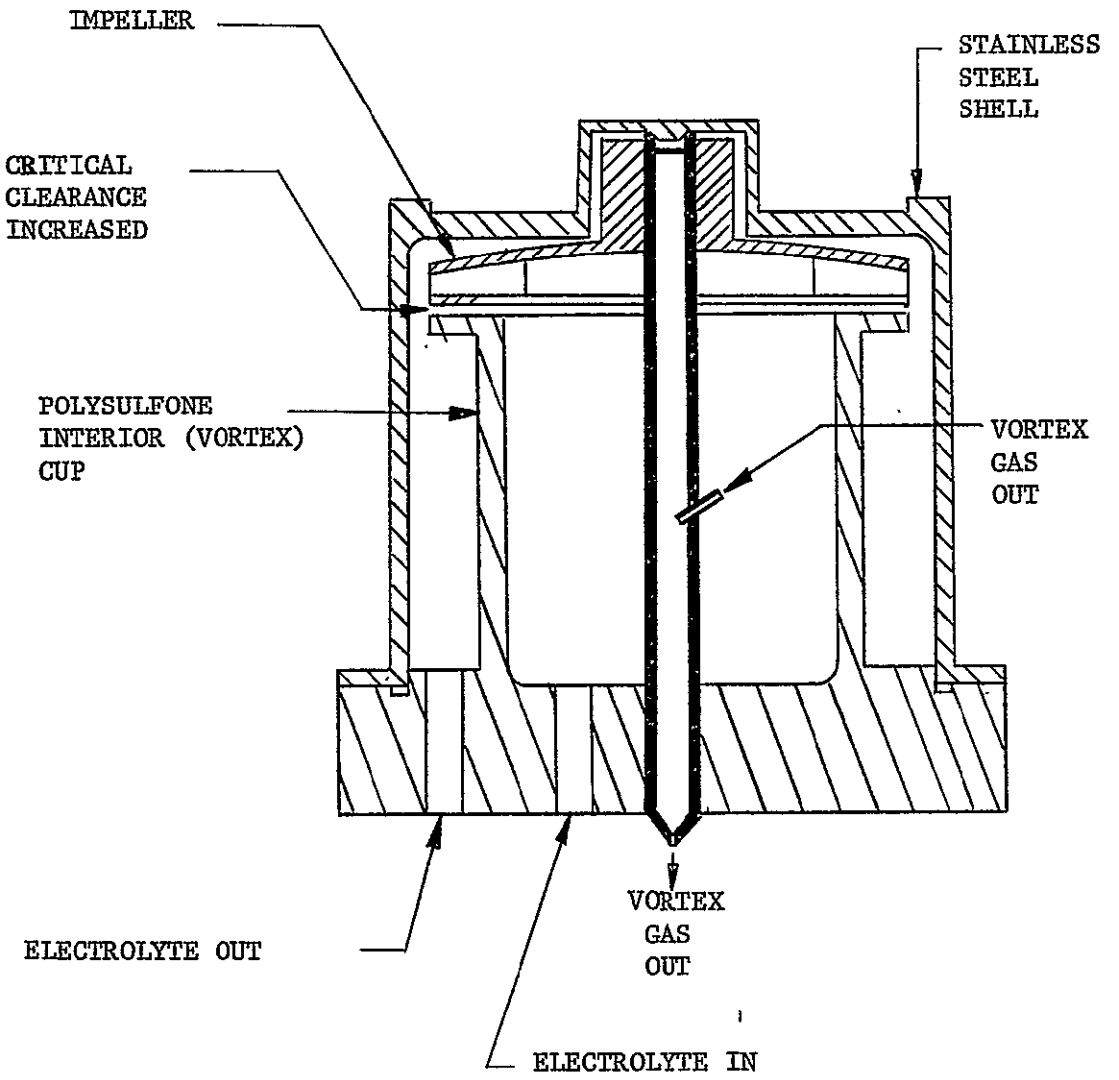


Figure 12 Pump/Bubble Separator

Two things were immediately observed: 1) the crack in the impeller which had previously been stop drilled and filled had restarted and 2) the back side of the impeller had been rubbing the pump shell. Localized heating from rubbing appeared to have caused the original crack to continue.

After discussing the problem with both the designer and the NASA contract monitor it was decided to return the P/BS to Fluid Dynamics Inc. for rework. The primary purpose of the rework was to replace all polysulfone parts (the interior cup and the impeller) with stainless steel parts. This would make all parts, having critical clearances, of the same material and the same thermal expansion characteristics. Once the rework was complete, no more problems were encountered.

It was noted throughout the term of this contract that the P/BS seems to have one shortcoming: it does not remove finely divided gas from the electrolyte stream. It is estimated that bubbles of less than about 0.01 in. diameter are only particially removed or not removed at all. After the smaller bubbles have coalesced into larger ones, the P/BS separates quite well.

2.4 Electrolysis System Testing

2.4.1 Parametric Tests

While the P/BS was being rebuilt, an external pump and bubble trap of the one "g" type were installed to allow continuation of the system parametric tests. The parametric tests had as their primary objective the determination of the effects of operating at elevated temperature up to 150°F. Secondarily, it was desired to determine the volume of hydrazine feed injections and the "burndown" time or N_2 production decay information which would be useful in a planned long duration system test.

The first series of tests were begun by heating the module to 150°F (66°C) with the electrolyte circulating but with no power applied to the cell stack. Heating was accomplished by routing the electrolyte through the

heat exchanger while pumping 180°F (82°C) water through the heat exchanger channels normally used for coolant. Once the electrolyte temperature reached 150°F (66°C), the heating/cooling system was switched to the automatic mode which was controlled by the base plate thermobulb.

As power was applied to the preheated cell stack large quantities of foam of unknown composition appeared in both the O_2 and H_2 gas spacers and was carried, via the Δ P regulators, into both gas bubblers. Only 5 amps (34 mA/cm^2) was applied. At the same time large quantities of gas appeared in the electrolyte, causing a rapid rise in electrolyte pressure and then an automatic shutdown by actuating the high level sensor in the reservoir volume controller. Analysis of the gas in the electrolyte identified it as predominately hydrogen.

After shutdown, the system was run in the N_2 purge mode with no power to determine if the gas was being formed in the electrolyte or was leaking through the membrane. There was no N_2 in the electrolyte and it was concluded that the gas was not "leaking" through the membrane.

The next runs were made after the module had been drained and flushed with fresh KOH two times. Also, the module was not preheated prior to the application of power. Rather, the inherent heating due to IR losses was utilized. Low mode current of 7.5A was applied first bringing the electrolyte temperature to about 85°F (29°C). High mode current of 21.75A then raised the temperature to 100°F (38°C). Finally auxilliary heat was added until the temperature reached 150°F (66°C). Cell voltages at this temp were quite satisfactory, averaging about 1.8 volts. This voltage was consistent from cell to cell.

This time there was no foaming but there was still gas in the electrolyte. In the low mode, the gassing rate was about 150 cc/hr while the high mode produced 300-900 cc/hr. This gas was composed of about 80% hydrogen

with the remaining 20% being oxygen, nitrogen and water vapor. The composition did not change between high and low mode. Succeeding runs with KOH only and utilizing automatic high/low mode operation produced gassing rates as high as 1400 cc/hr with the same composition as before.

Since the temporary bubble trap was removing most of the gas from the electrolyte, a hydrazine injection was made. The objectives of this run were: 1) to see if hydrazine addition increased the gassing rate, 2) to see if the composition of the gas changed, 3) to start gathering data for the determination of proper hydrazine injection volume, and 4) to acquire data on N_2 production rise and decay profiles. With respect to 1) and 2) the gassing rate did increase and the composition did change. The quantities of hydrogen and nitrogen were about equal at 45% each with the remaining 10% being oxygen and water vapor. Small amounts of data were gathered toward 3) and 4) but were insufficient even to verify the previously run single cell hydrazine efficiency tests.

A second significant event occurred with the addition of hydrazine: finely divided black particles appeared in the electrolyte. A sample of these particles were analyzed and found to be predominately carbon black with some platinum black. These particles were present in sufficient quantities to make the electrolyte opaque and dark grey in color. The particles settled out in the bubble trap only after power to the cell stack was removed, indicating that fine gas bubbles were carrying the carbon and platinum particles. Evidently the particles began settling out of the electrolyte after the gas was vented off but while the electrolyte was still being circulated.

At this point because of funding limitations, it was decided to begin the long duration testing of the system.

2.4.2 Long Term Test

The long term test was started in the low current mode to take advantage of the consequent low heating rate and hopefully low gas production rate. However, considerable gas (predominately hydrogen) immediately appeared in the electrolyte. Although the newly rebuilt and reinstalled P/BS easily removed the gas, the gas displaced sufficient electrolyte to cause a "high electrolyte" shut-down. A quantity of electrolyte roughly equal to that displaced by the gas was drained from the system and a restart was made. It was then necessary to add or drain electrolyte until the volume of gas stabilized. This precluded unattended running since changes in gassing rate (within the electrolyte) caused high or low electrolyte shut-downs. Gassing rate changes occurred at each transition from low to high (current) mode operation. High mode produced more electrolyte gas than did the low mode.

A 50 cc hydrazine injection was made to determine its effect on gassing rate. The effect was quite dramatic: 12 liters per hour were measured for low mode while the high mode produced 28 liters per hour. The large quantity of gas forced the termination of the test. Subsequently, three tests were run to determine if the gas was generated or the result of leakage. These tests included 1) running the stack on reversed polarity, 2) running only half the cell stack at a time and 3) purging the cell stack (no power) alternately with hydrogen and oxygen. The results of these tests indicated that the gas was being generated rather than leaking through the membranes.

2.5 Investigation of Gassing Problem

2.5.1 Half Cell Tests

As a result of the gassing problem encountered throughout the system testing a "problem solving" session was held with Dr. T. Katan of Lockheed's Palo Alto research facility. The purpose of this session was to: 1) identify the most likely source(s) of the hydrogen gas in the module electrolyte; 2) define tests which could determine the specific source(s); and 3) develop a plan to correct the problem.

These discussions identified the most likely source of the extraneous gas as the stainless steel membranes located between the electrodes. Previously, nickel screens had been used for the same function and had not caused such gassing with KOH and H_2O. However, hydrazine manufacturing evidently uses only stainless steel while nickel was indicated to be autocatalytic for hydrazine. Still the test circumstances pointed to the stainless steel membrane as the most likely source of the extraneous gas.

This then raised the question of why was stainless steel functions contrary to previous experience with nickel screens. The supposition was made that relative motion between the stainless steel membrane and the electrode was caused by the thermal cycling of the cells in the initial parametric system test at 150°F (66°C) and high current. Buckling stresses might then disturb the insulation around the periphery of the membrane or more likely the asbestos which separates and also insulates the membrane and the electrode. Areas of lowered resistance and even shorting might occur.

To test this assumption two independent "half cell" tests were devised. The first test was to be a small scale one fabricated and tested by Dr. Katan in this laboratory in Palo Alto. The second test was to be one with full scale module cell stack parts, fabricated and tested by LMSC Biotechnology at Sunnyvale. The full scale, half cell tests showed conclusively that hydrogen could be generated at the surface of the stainless steel membrane in the electrolyte. However, it appeared that only specific areas on the membrane surface produced gas. These areas were probably where gas (H_2) breakthroughs had occurred previously due to excessive gas/electrolyte ΔP generated at the high temperature, high current start-up condition. These same areas also coincided with "thin" areas of asbestos. Figure 13 shows the Biotechnology laboratory set up for the half-cell test.

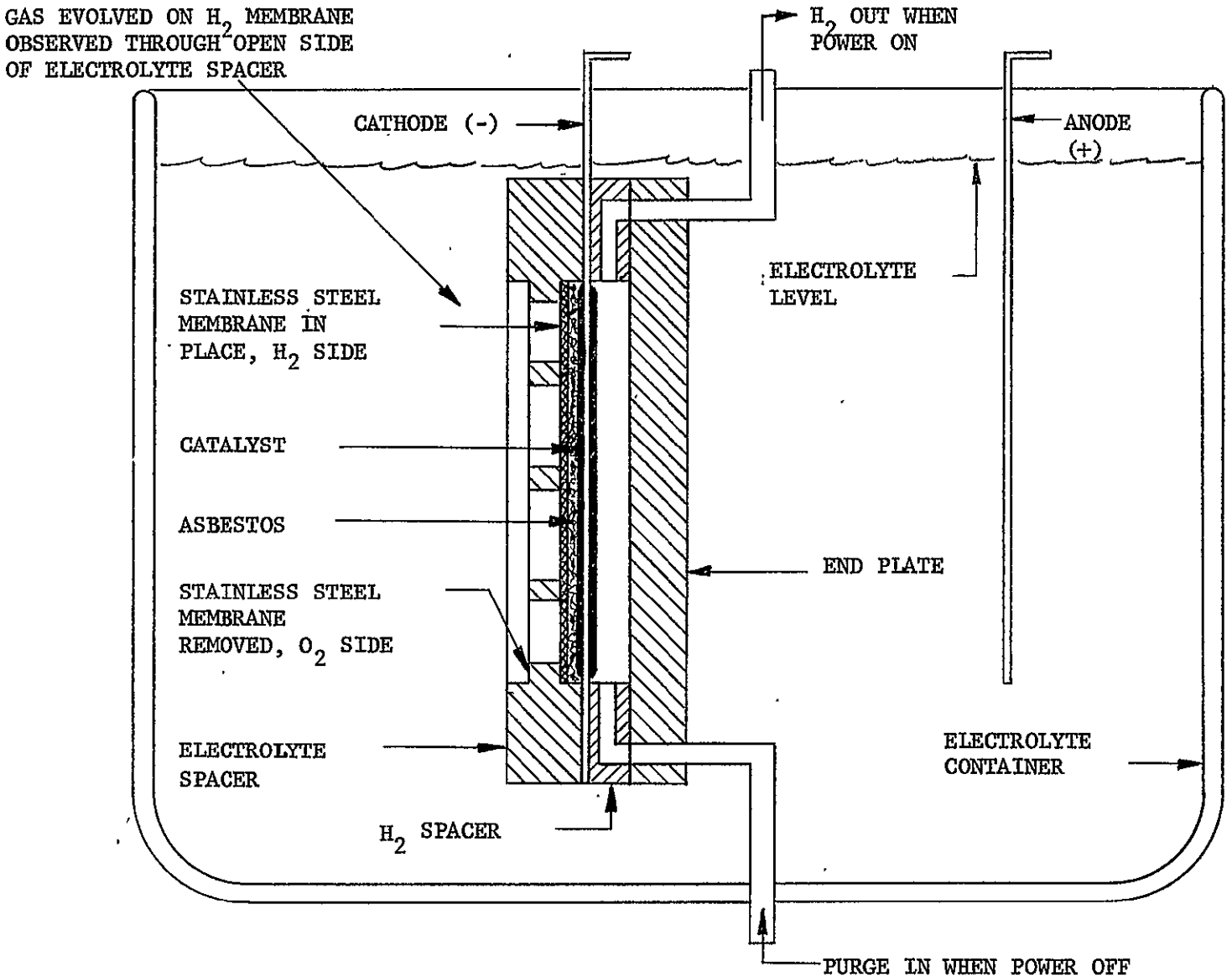


Figure 13 Half Cell Test Configuration

Dr. Katan's investigation identified a reasonable explanation of how the localized gassing could occur even after the initial gas breakthrough conditions were changed. His report is included as Appendix A.

2.5.2 Full Cell Design Modifications and Testing

Because of funding limitations it was necessary to find a solution to the gassing problem in the most expeditious manner possible. Consequently, a basic, broad based approach was not feasible at this time.

The first concept was to insert a thin nonmetallic membrane such as PVC between the stainless steel membrane and the asbestos. Besides adding insulation between the electrode and the stainless steel membrane, the PVC would also enhance the phase separation capability of the membrane/asbestos/electrode laminate. Also, it was expected to raise the potential of the cathode.

In preparation for the build-up of a single cell to test the above "fix" a new asbestos application procedure was developed. Instead of applying the asbestos directly to the electrode it was applied to the PVC membrane. Application of asbestos to the electrode had always produced rather uneven porosity of the cathode, which caused the asbestos to accumulate in areas of higher pososity during the slurrying process.

The porosity of the PVC, on the other hand, is very consistent so that the water in the slurry drains through the membrane evenly, leaving an asbestos coating of exceptional thickness consistency. This method of asbestos application was used throughout the remainder of the program.

A single cell was assembled for the purpose of testing the PVC membrane/asbestos laminate. No cell structural modification was necessary. The PVC membrane/asbestos assembly was simply captured between the stainless steel membrane and the electrode which had almost all of the asbestos removed that had originally been applied to the electrode.

2.5.2.1 Temperature Cycling

The modified single cell was first run for approximately 60 hours at temperatures varying between 75°F (24°C) and 95°F (35°C). The cell performed satisfactorily except that the cathode voltage was twice the voltage of previous cathodes. This increase was somewhat more than expected. Raising the electrolyte control temperature from 75°F (24°C) to 95°F (35°C) resulted in a cathode voltage improvement of about 0.2 volts. In spite of this improvement cell voltages are still in excess of 2.0 volts at temperatures less than about 140°F (60°C). Since the higher temperatures seemed to be causing problems with the stainless steel screens and increased gassing when using hydrazine, it became necessary to expand the scope of the modified single cell testing.

2.5.2.2 Stainless Steel With and Without PVC

A total of nine additional single cell tests were planned with the following objectives:

1) Reduce cathode voltage;
2) Reproduce the shorting phenomenon in those cells using the stainless membrane (+PVC):
3) Determine if using an anode as a cathode effected hydrazine efficiency;
4) Determine the effect of removing the stainless steel membrane but retaining the PVC on voltage and gassing, with and without hydrazine.

The cell configurations used in the first tests were as follows:

1. Anode as cathode, stainless steel membrane, no PVC membrane, and standard asbestos loading on the electrodes (baseline).
2. Anode as cathode, stainless steel membrane, PVC membrane, light asbestos loading on the PVC membrane.
3. Anode as cathode, stainless steel membrane, PVC membrane, and standard asbestos loading on the PVC membrane.
4. Cathode as cathode, stainless steel membrane, PVC membrane, and light asbestos loading on the PVC membrane.

The standard asbestos loading weighs 1.55 gms while the light loading weighs 1.0 gm. One gram of asbestos is the minimum amount that can be evenly slurried over the required area of 145 cm^2. Note that, where used, the PVC membrane was used in addition to the existing stainless membrane and support screen.

The lowest cell voltage, other than that from the baseline cell (#1 above), was produced by the #3 configuration. Its standard or heavier asbestos loading produced somewhat lower voltages than the lighter loadings because the heavier loading provided a better electrolyte path, that is, better wicking. Voltages for the standard and light loadings were essentially the same above 125°F (52°C).

Cell voltages below 2.0 volts were obtained only above 140°F (60°C) except for the baseline cell which required 110°F (43°F) to achieve 2.0 volts. Configurations 2), 3), and 4) were temperature cycled in an attempt to produce shorting but none occurred.

Configuration 2) was run with a 2M charge of hydrazine to determine voltage and gassing characteristics. The charge was added when the electrolyte temperature was about 100°F (38°C) and rising. With the addition of hydrazine, cell voltage rose immediately to 2.75 volts, then decreased as the temperature increased. The lowest cell voltage, 2.45 volts, was achieved at 150°F (66°C) although there was little voltage change between 135°F (57°C) and 150°F (66°C). This may have been due to gas in the electrolyte partially blanketing the membrane and counteracting the usual temperature effects.

Gas in the electrolyte became evident and measurable (95 cc/hr) at about 135°F (57°C). At 150°F (66°C) the rate had increased to 700 cc/hr which would be about 15.5 l/hr for a full cell stack. Analysis of the gas in the electrolyte (at 145°F)(63°C) showed 27.3% H_2, 7.2% O_2, 65.5% N_2 while the cathode side gas out showed 74% H_2, 4% O_2 and 22% N_2.

2.5.2.3 PVC Membrane Only

The remaining tests were run in an attempt to locate the source of gassing observed in the previous hydrazine tests. This gassing, besides occurring with the addition of hydrazine, was observed to increase with electrolyte temperature. Since heat was introduced to the electrolyte at the stainless steel heat exchanger and since gas was observed in the heat exchanger outlet lines, the stainless heat exchanger was replaced with a plastic one for two of the tests. Tests 6, 7, 8 and 9 were configured as follows:

6. Anode as cathode, stainless steel membrane and support screen, PVC membrane, light (1.0 gm) asbestos loading on PVC, and stainless heat exchanger.
7. Anode as cathode, stainless steel membrane and support screen removed, PVC membrane with nickel support screen, standard (1.55 gm)
8. Same as 7. except plastic heat exchanger.
9. Same as 8. except cathode as cathode.

Configurations 8) and 9) produced very little gas in the electrolyte even though the control temperature was 150°F when the hydrazine was added. Also there was little difference in hydrazine efficiency between using an anode or a standard cathode as the cathode. There were, however, voltage differences. Tests 8 and 9 "hydrazine" voltages were comparable with the previous "KOH only" voltages at all temperatures.

It was therefore decided to retest the prototype module using a ten (10) cell stack. The cells were configured as in 8. above. Only ten cells were used because anodes were used as both anodes and cathodes and only 20 useable anodes remained from the previous cell stack. Fabrication of new electrodes would have consumed the remaining funds. This short stack module was tested to the extent allowed by the remaining contract funds.

2.5.2.4 Ten Cell Module Test

Although no problems were encountered during the assembly of the cell stack, several problems arose with peripheral components when start up of the module was attempted. The problems were minor but time consuming.

After start up of the module, a reservoir failure was indicated by the fact that neither automatic or manual water feed produced any change in the electrolyte level (volume) indicator. However, water was being injected as evidenced by the decreasing level in the feed tank. The unit was immediately removed and checked for leaks in the Bellofram but none were found and there was no electrolyte on the gas side. This meant that either the piston position sensor or its associated, external electronics had failed. The reservoir was refitted "as is" and water feed was accomplished by timed, manual injections.

Also, the pump/bubble separator (P/BS) stopped venting gas. The vent valve operated in the manual mode but remained open in the automatic mode. It was suspected that the vortex sensor pick-up had failed since it had done so previously and in a like manner. It was not replaced since all spares had been used. The small amount of gas produced in the electrolyte was vented manually.

The two purge gas solenoid valves stuck open but did not effect the test as manual shut off valves had been previously installed in series with them.

The malfunction that finally terminated the test was in the cell stack power supply. During the test it had dropped out intermittently, apparently due to overheating. It finally quit completely and so terminated the test.

The final prototype module test ran for about 5 hours. No hydrazine was injected due to the failure of the cell stack power supply. The cell stack was run at 21.75A (150 m/A/cm^2) and 150°F (66°C). These conditions produced

cell voltages averaging 1.72 volts with a standard deviation of 0.02 volts. Cell voltages averaging 1.89 volts were achieved at 21.75A and 90°F (32°C). This concluded the prototype module testing.

2.6 Feasibility Study of Generating 100% Nitrogen

A study was performed to determine the applicability of the LMSC O_2/N_2 electrolysis technology to the generation of nitrogen for spacecraft inerting and safety purposes. The study identified three possible operating modes of the circulating electrolyte system that may have merit as first stages in a system design that would generate 100% nitrogen as one product. These modes were:

- Operation at zero potential (possibly in a different configuration) to decompose hydrazine but without production of ammonia;
- Operation at a potential to yield a H_2/N_2 effluent with a relatively high concentration of N_2;
- Operation at a potential to yield an O_2/N_2 effluent with a relatively high concentration of N_2.

The actual selection of the most favorable operating mode will depend upon an evaluation of system penalties and qualitative operational parameters. In each of the above cases, a second electrochemical purification stage is required to obtain pure nitrogen. Depending on the selected first stage operating mode, the purification stage may involve either separation of H_2 and N_2 or O_2 from N_2. In order to make a final judgement of the best approach additional testing of the LMSC system will be required.

In order to place the subject of spacecraft nitrogen supply in proper perspective, data on possible supply methods were gathered. Nitrogen is lost to space through vehicle leakage and purging or inerting of equipment. Since these losses of nitrogen are irreversible, all nitrogen must be brought to orbit and stored until ready for use. Regeneration, as in oxygen from carbon dioxide, is not possible. The commonly considered methods of nitrogen supply are:

- o Gaseous
- o Cryogenic
  - subcritical
  - supercritical
- o Chemical
  - hydrazine
  - ammonia

In the case of the gaseous and cryogenic supplies, all the stored material except a small residual is available for nitrogen supply. The chemical sources include hydrogen. If the hydrogen is of use, as in a Sabatier reactor for oxygen recovery, the penalty on a chemical supply systems may be reduced.

The key parameters in the selection of a nitrogen supply system include:

- o Total equivalent weight
- o Cost
- o Safety
- o Delivery pressure
- o Value of hydrogen

Since some of these parameters can not easily be quantified, part of the final selection decisions will be qualitative in nature.

The vehicle mission is also of importance in that it may have a significant effect on the trade-off parameters. Important considerations are:

- o Total mission duration
- o Resupply period
- o Power penalty
- o Interface constraints

The first step in the study was the establishment of delivery system requirements. A number of sources of data are available for long mission duration

vehicles. The SSP study is one of the most recently completed and was adopted as the model for much of this work. In addition, other studies were examined to determine the nitrogen supply requirements used. The following is a summary of the trade-off criteria and data sources.

- o Nitrogen requirements:

  4#/day nitrogen supply for atmospheric make-up (Martin)
  2#/day of pure nitrogen for purge and inerting (Martin)

- o Mission duration

  Variable from 30 days to over 1 year

- o Power penalty

  Continuous 591 #/KW (SSP)
  Day light 151 #/KW (SSP) 54 minutes of 94 minute orbit

- o Hydrogen value

  None - either Bosch or solid electrolyte O_2 reclamation system assumed

- o Spacecraft venting

  Undesirable - possible surface contamination

Other studies used the following nitrogen generation requirements:

Battelle electrochemical	15#/day
Life Systems Inc.	15#/day
Allis-Chambers I	2-29.4 #/day

With these general design criteria and design parameters, the penalties associated with each storage method were examined. The results follow.

Gaseous Storage

The simpliest approach to nitrogen storage is storage as a high pressure gas. This storage technique has a number of advantages which include:

- o Simple system
- o Well developed
- o Safe
- o Instant gas availability in any quantity
- o High pressure delivery

- o Minimum vehicle interfaces
- o Indefinite stable storage

Offsetting these advantages are:

- o High penalty (weight)
- o Large volume

A wide range of penalty numbers are presented for gaseous storage. Some of these are:

o 1.15 # system/#N_2	MARS/MOSS	Ti tank
o 0.46 # system/#N_2	AILLS	filament wound tank
o 1 - 1.4 # system/#N_2	Shuttle	

It seems, on the basis of the above ranges, reasonable to present both a 0.5# system/N_2 and 1.3 # system/N_2 curve in a comparison study to show best possible (high development cost) and readily obtainable (modest development) penalty numbers.

Cryogenic Storage

The storage of atmospheric gases in the cryogenic state is a well developed concept. The main developed effort to date has been the storage of oxygen. However, the same principles apply to nitrogen storage. Cryogenic storage has the following advantages:

- o Low penalty
- o High pressure delivery possible
- o Low system volume
- o Developed technology

Offsetting these advantages are the following disadvantages:

- o High cost
- o Excessive energy required for high delivery rate
- o Modest integration problem - vehicle cooling interface
- o Minimum boil-off rate prevents extended storage

Possibly the greatest limitation to cryogenic storage for extended missions relates to boil-off due to heat leak into the tank. If minimum penalties are to be realized, the boil-off must not exceed the use rate. As mission times increase, the tank size will increase and use rates will stay the same. Thus, it can be seen that the tank area and amount of insulation increases and the ability to meet the minimum boil-off rate becomes increasingly difficult. It appears that nitrogen storage beyond 180 days would not be feasible for a 7 #/day use rate.

Two forms of cryogenic storage have been investigated. These are supercritical and subcritical. The subcritical storage, (storage below the critical pressure) has a slightly lower penalty but is more difficult to implement. However, as penalty differences between these two approaches are close the use of a single representative number was selected for this study. The following typical penalty numbers are found in the literature:

o MARS/MOSS	0.1 #/hr use	0.32 # system/#N_2
o Shuttle	0.4 #/hr use	0.21 # system/#N_2
	0.15 #/hr use	0.35 # system/#N_2

Based upon these penalties, the following values were selected for this study:

0.35 # system/#N_2	180 day missions
0.28 # system/#N_2	90 day missions

As previously discussed cryogenic storage could be used beyond 180 days at increased penalty. This was not explored in this study due to uncertainties in the penalty numbers.

The crogenic penalty data can be extended beyond 180 days if the maximum resupply cycle is less than 180 days. In this case the attractiveness of cryogenic supply would be significantly enhanced.

Chemical Storage - General

High density ambient pressure and temperature storage of nitrogen is possible when stored as a chemical. Possible storage chemicals which have been examined include:

- o Hydrazine (N_2H_4)
- o Ammonia (NH_3)
- o Azides (e.g. LiN_3)

The azide chemicals are especially hazardous and are not considered feasible. Work has been done on both hydrazine and ammonia.

The quantity of chemical required per # of N_2 delivered is calculated as follows. As previously discussed, no credit is taken for the possible value of hydrogen associated with these chemicals.

- o N_2H_4 1.143 # chemical/#N_2
- o NH_3 1.214 # chemical/#N_2

Considering that the penalty for water tankage is about 0.15 # tank/# water and that storage of these chemicals is similar to the storage of water, a correction can be made for actual storage density. This results in combined storage penalties of:

- o N_2H_4 1.313 # chemical + storage/# N_2
- o NH_3 1.436 # chemical + storage/# N_2

These penalty numbers represent a "base" penalty for the chemical storage of nitrogen. Any equipment required to reclaim the nitrogen must be added to these penalty values.

At this point we can make a comparison of nitrogen supply on the basis of storage alone. Figure 14 presents the combined nitrogen and system weight penalty for the storage of nitrogen as a function of mission time. The basis selected for this figure and the ones to follow was 7 #/day of nitrogen. The

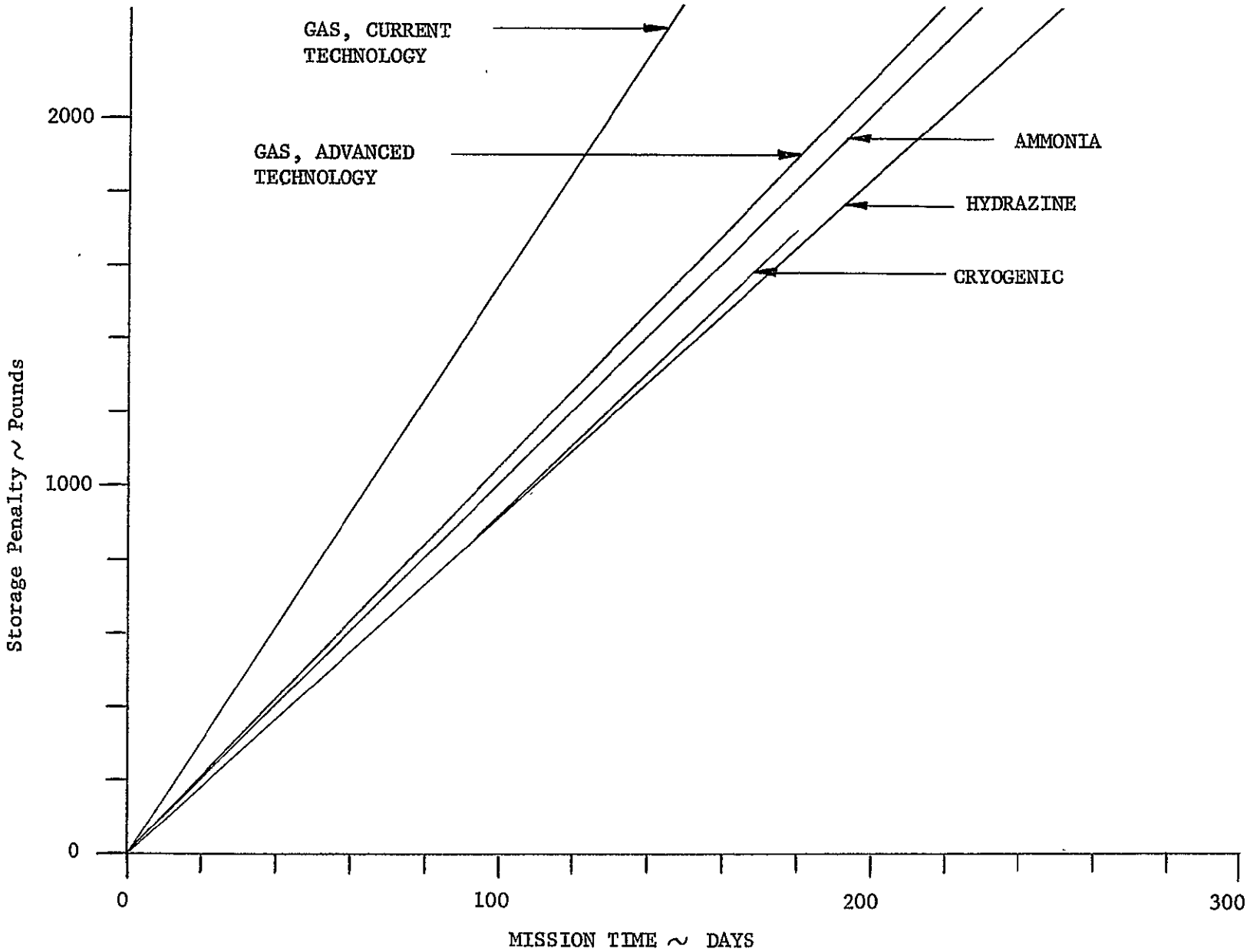


Figure 14 Nitrogen Storage Penalty

figure shows that cryogenic supply of nitrogen is a clear choice over other methods if the use rates are sufficiently high and the mission time sufficiently short to prevent excessive boil-off. For short missions (less than 30 days), the additional penalty for gaseous tankage is sufficiently small so that this type of storage would likely be favored. In summary, the likely system choices for nitrogen storage can be summarized as follows:

- o 0 to 30 days — gaseous storage
- o 30 to 180 days — cryogenic storage
- o 180 days plus — chemical supply

These general conclusions will vary somewhat with mission specifics but they do indicate that chemical supply of nitrogen is most feasible for very long duration missions. Further, when resupply is considered, cryogenic supply may be favorable even beyond a mission of 180 days.

Chemical Storage - Implementation

All methods of pure nitrogen supply from a chemical source include the following two basic steps.

- o Chemical decomposition
- o Nitrogen separation

Each of these process steps can be considered in turn.

Decomposition - The first step in nitrogen from a chemical source supply involves the decomposition of the chemical to nitrogen and hydrogen. This step is currently carried out at elevated temperatures in the presence of a catalyst.

In the case of hydrazine, decomposition to nitrogen, hydrogen, and ammonia is easily accomplished and rapid. The main effort in the design of a decomposer lies in the reduction in ammonia to the lowest possible level. It is desirable to provide nitrogen at about 150 psi to minimize storage volume

for the purge nitrogen supply. Therefore, decomposition at 200 psi seems desirable. This will provide 150 psi after the purification steps. If decomposition is carried out at 200 psi, the corresponding equilibrium quantities of ammonia leaving the decomposer will be:

- o 0.2% at 1340°F (727°C)
- o 0.45% at 1160°F (627°C)
- o 1.2% at 980°F (527°C)

At these temperatures, decomposition over a catalyst is rapid and equilibrium is rapidly approached. However, during the quench from the reaction temperature, reforming of ammonia will take place. In a practical sense, development programs to date indicate ammonia levels as low as 0.5% may be possible. However, the data show 2-2.5% ammonia is typical of the current achievable levels. This ammonia must be removed before the nitrogen can be delivered. The separation processes used for the removal of hydrogen will not remove ammonia.

One method of ammonia control commonly used is chemisorption. Either the adsorption by phosphoric-acid-treated charcoal or copper sulfate on sorbeads is feasible. Depending upon the extent of adsorption which can be achieved with these high ammonia levels, the quantity of sorbent will be in the range of 10 to 15 gm sorbent/gm NH_3. Assuming that 1% ammonia can be achieved with additional development, the impact of the ammonia adsorption requirement is significant on the chemical storage system penalty. Figure 15 shows the impact of 1% and 2% ammonia on hydrazine storage. The additional penalty is for ammonia control only. A sorbent quantity of 14.7 gm sorbent/gm NH_3 was used. No hydrogen purification penalties are included as yet. Figure 15 clearly shows the need to achieve low ammonia levels in the decomposer.

An estimate of the penalty of a hydrazine decomposer was made based on reports by Allis Chalmers and Life Systems. A weight of 10 pounds and a power of 30 watts seems likely. The power is required to maintain the unit at temperature.

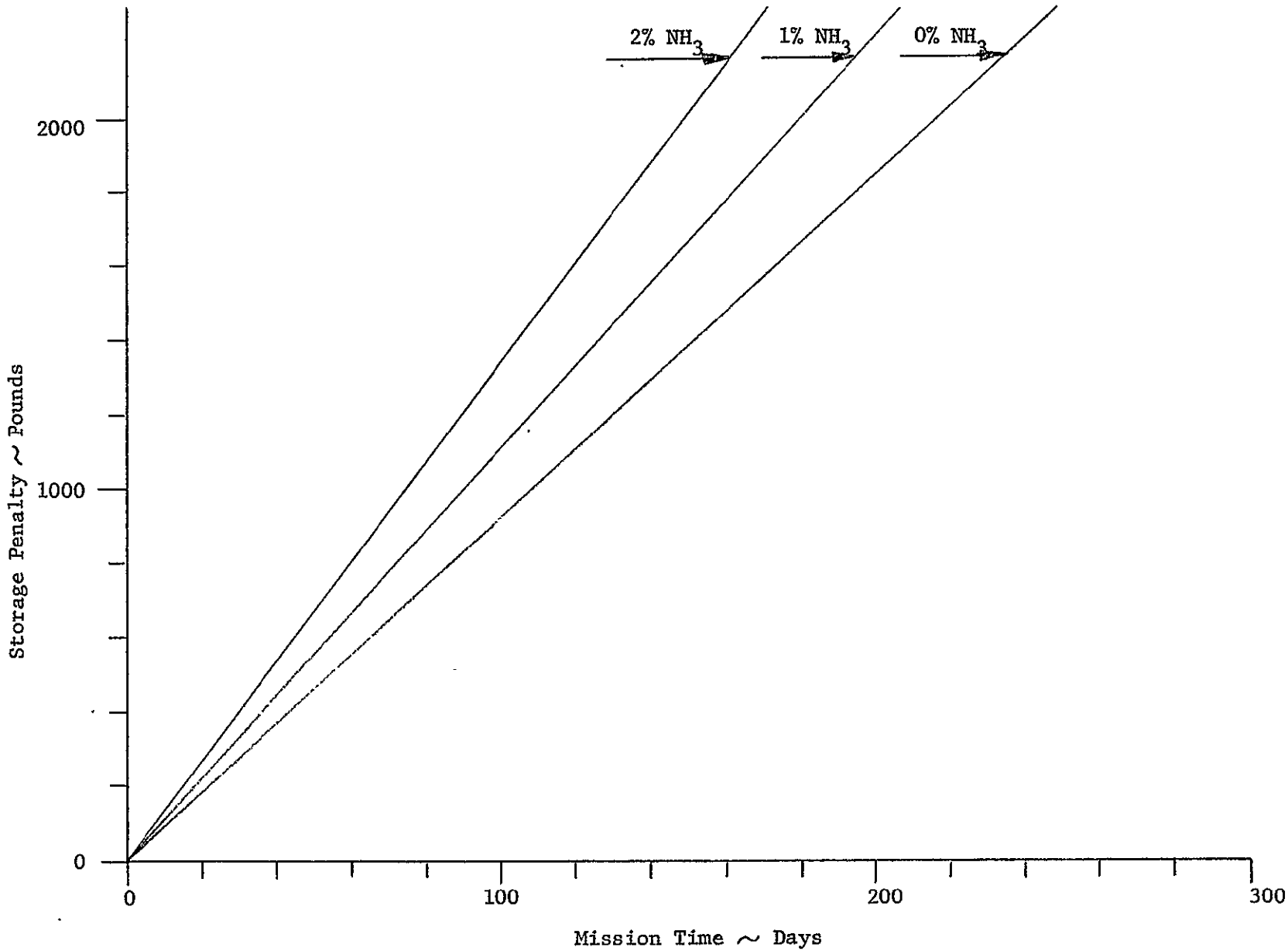


Figure 15 Hydrazine Storage Penalty Corrected for NH_4 Control

Following decomposition of the stored chemical, separation of the hydrogen from the nitrogen is required. Two methods have been investigated. These are:

- o Membrane diffusion
  - polymer (Life Systems)
  - Pd/Ag Life Systems and others)

- o Electrochemical
  - Pd/Ag electrode (Battelle)
  - Pt electrode (Life Systems, AC)

A multistep combination of methods seems optimum.

Looking at the electrochemical technique, some insight is possible in determining the final system selection by defining the amperage required. The separation of 7 #/day of nitrogen resulting from the decomposition of hydrazine will require at least 507 amps. This is derived as follows:

$$N_2H_4 \qquad N_2 + 2H_2$$

The electrochemical separation of $2H_2$ will require the transfer of four electrons thus:

$$\frac{(7)(453.6)}{(24)(3600)(28)} = 0.0013125 \text{ gm mols } N_2/\text{sec}$$

$$(.001325)(4)(96500) = 507 \text{ amps}$$

Now we may consider the power required for electrochemical separation.

Where the hydrogen concentrations are high, the separation can be accomplished by as little as 0.1 volts. However, as the concentration of hydrogen decreases, the required potential to separate hydrogen may rise to as high as 0.50 volts. If a nominal value of 0.15 volts is considered, the energy required to separate the hydrogen will be in the order of 75 watts at 100% current efficiency.

An advantage of the electrochemical separation is the high purity possible and the ease of monitoring and control. Thus, combination with a lower penalty first stage membrane separation process seems desirable to reduce the power requirements. Both the polymer and Pd/Ag membrane separators are capable of 85% removal of hydrogen in a single stage. The nitrogen rich product is delivered at near the decomposer pressure of 200 psi. The energy for separation is provided by the pressure in that the hydrogen is delivered at 25 psi. If a higher hydrogen delivery pressure is desirable as in the case of its being useful, the higher penalty of an electrochemical separation which would deliver both streams at pressure may be justified. Otherwise the low penalty of membrane first stage separation seems the best approach.

The polymer membrane separator will have a small fixed weight and will require no power. It should be noted that current polymer membranes are not compatible with ammonia.

A Pd/Ag membrane operates best at elevated temperature, around 700°F 371°C (700°F). Thus, although the fixed weight will likely be low, a power penalty in the order of 20 watts seems likely to maintain the temperature of the unit.

The combination of a first stage polymer membrane separation will reduce the penalty of the electrochemical separator by as much as 50 watts. This seems most desirable.

In summary, chemical nitrogen supply system will likely consist of the following components.

- o Chemical decomposition
- o Ammonia control
- o Membrane 1st stage (85%) hydrogen separation
- o Electrochemical purification
- o Catalytic Oxidation (final hydrogen cleanup)

The following is considered as typical penalty breakdown for such a process which uses a polymer membrane first stage separator (Life Sciences) and a Pd/Ag electrode (Battelle) electrochemical cell.

	Weight	Power
Decomposer	10 lb	30 watts
Polymer Separator	8 lb	0
Electrochemical Separator	12 lb	25 watts
Ammonia Control	(See Figure 17)	
Catalytic Oxidation	(Normal part of ECS)	

A total penalty of 30 lbs and 55 watts might be expected. At 591 #/KW this gives a total equivalent weight of 62 lbs. Use of the intermittent penalty is not indicated as power is required to maintain component temperatures.

Figure 16 presents the TEW penalty for this system as a function of mission time for a hydrazine feed and a decomposer which gives ammonia. Curves are included for both 1% and 2% ammonia.

Circulating Electrolyte Technology

Over the past several years, Lockheed has been carrying out investigations on oxygen/nitrogen generation systems which use hydrazine as a source of nitrogen. The Lockheed approach uses conventional circulating electrolyte electrolysis technology. The hydrazine is fed into the electrolyte as nitrogen is required. The result of electrolysis at voltages above 1.5 volts with hydrazine in the electrolyte is an O_2/N_2 mixture which can be used for cabin makeup nitrogen. The O_2/N_2 mixture contains no ammonia. By careful cell design, the decomposition of hydrazine at the cathode should be kept as small as 10 percent. This loss will appear in the hydrogen discharge. Currently, decomposition voltages are in the range of 2 volts. Additional development may lowet this to the 1.8 volt level. The resultant penalty of the LMSC system is seen in Figure 17. This includes a 10% hydrazine loss and power penalty calculated at both 0.591 and 154 #/KW. A

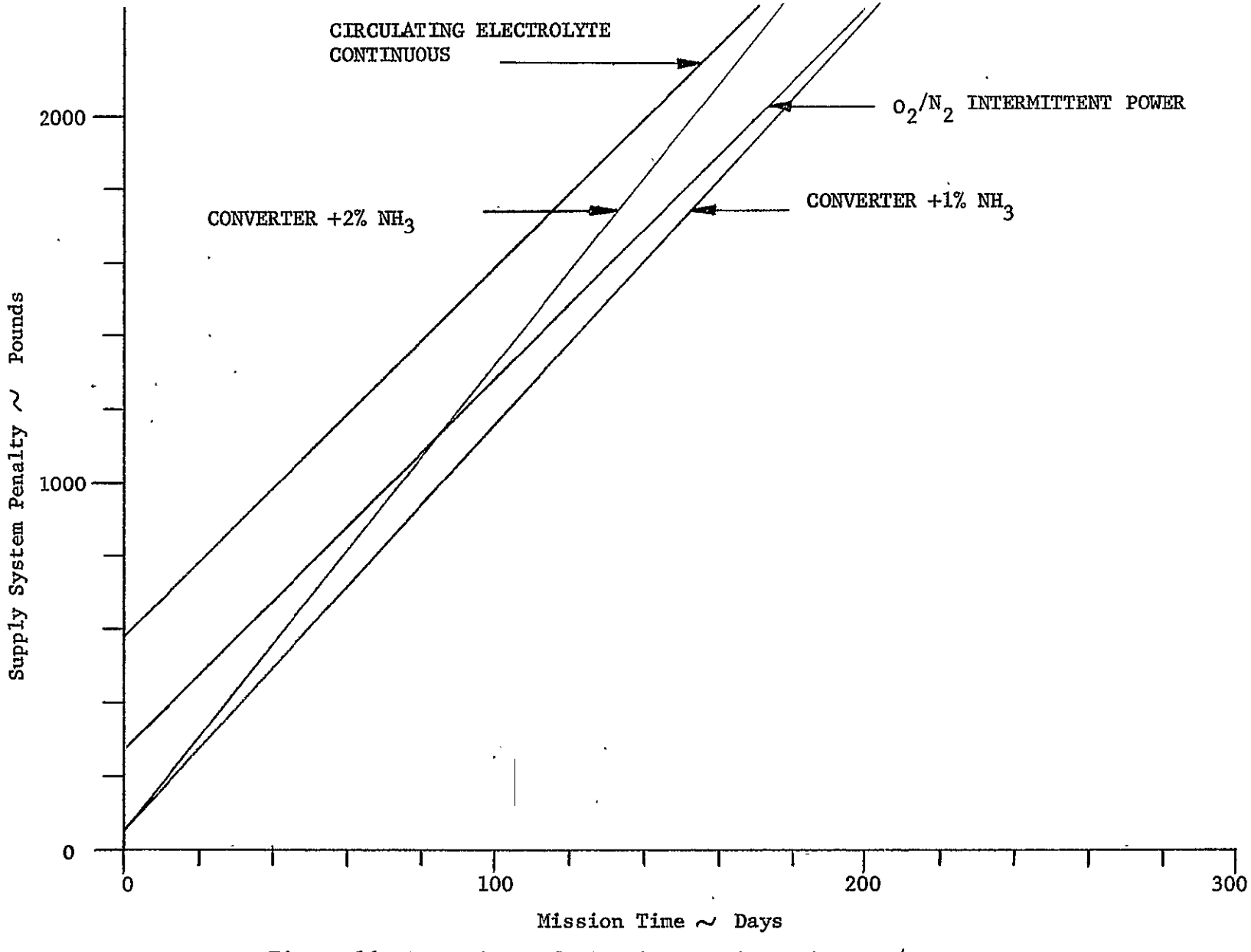


Figure 16 Comparison of Circulating Electrolyte O_2/N_2 vs Other Systems

value of 507 amps was used as the basis for calculation. In the case of the intermittent penalty, the amperage was adjusted by the assumed orbit characteristic of 54 minutes day light/95 minutes total. The intermittent operation is justified for the LMSC approach as all operations are at ambient temperature.

Figure 16 shows that operation of the LMSC O_2/N_2 system is only competitive at long mission durations. This is due to the problem of ammonia control with the other approach. If ammonia could be reduced to zero, as may be possible with an LMSC type unit operating at zero potential, combination with the other purification systems would have a lower penalty than the O_2/N_2 system.

As the voltage of the O_2/N_2 cell is dropped, the anodic effluent composition becomes increasingly rich in nitrogen and low in oxygen. At some voltage oxygen will go to zero and hydrogen will appear. As voltage is further dropped to zero, the ratio of nitrogen to hydrogen will approach 1:2. The presence of the high hydroxyl ion concentration will suppress the ammonia level to near zero. Thus, it can be seen that the possibility exists of developing a new hydrazine decomposer based upon LMSC electrolysis technology. Such a system would feed hydrazine to a circulating basic electrolyte loop. The hydrazine would decompose in the presence of a catalyst to form an ammonia-free N_2/H_2 mixture. This process can be carried out at ambient temperature and at a significant penalty savings as can be seen in Figure 17. The data presentation in Figure 17 is based on the previously discussed decomposer and a new design of the LMSC unit which would consume negligible power and weigh about 20 pounds.

Operation of the LMSC system at low voltages will result in an ammonia free nitrogen rich mixture at the anode. The effluent from a cell operation in this mode would require less purification than the gas from a normal chemical decomposer.

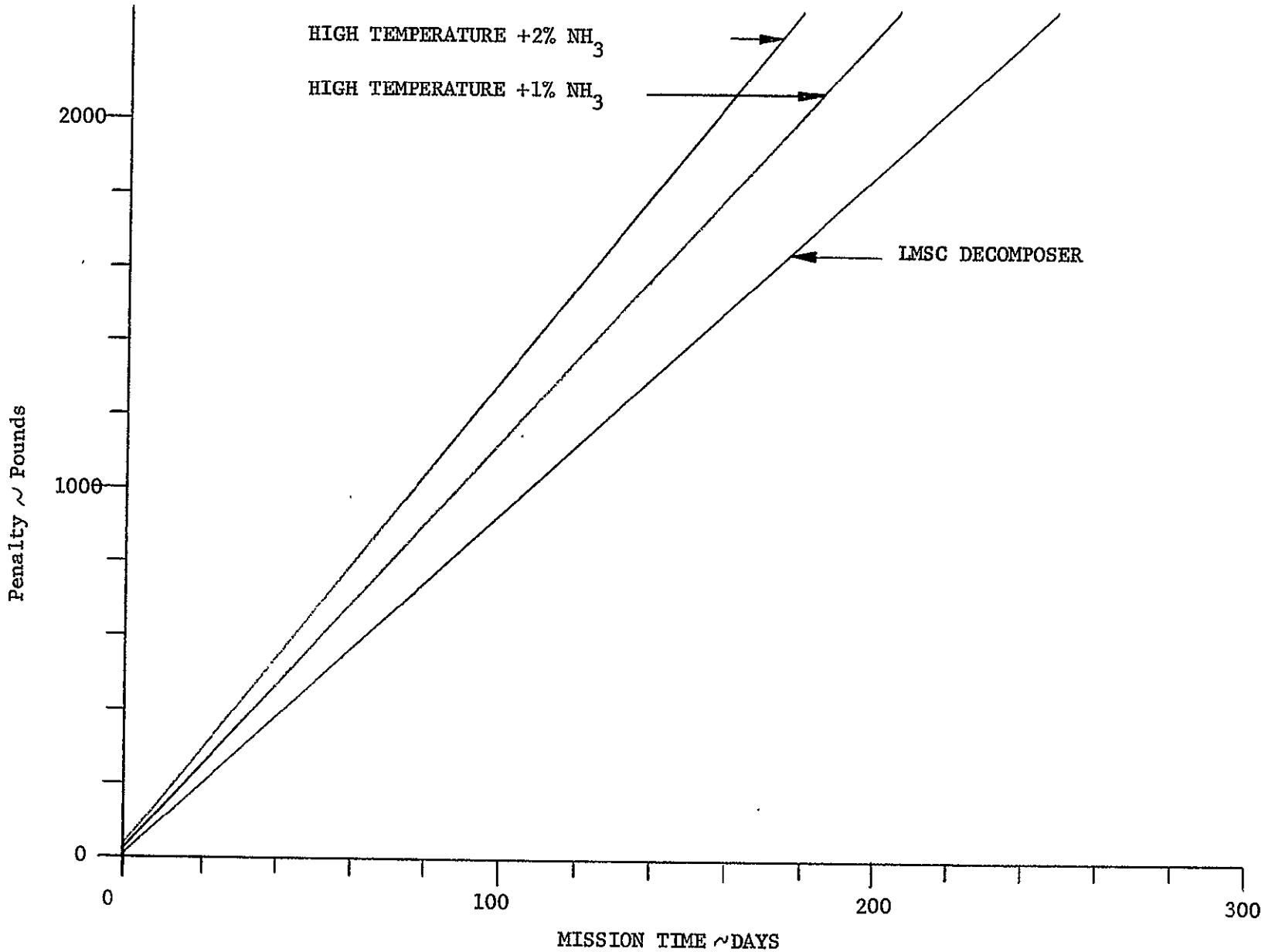


Figure 17 Penalty Comparision High Temperature vs LMSC Decomposer

In any of these possible operating modes of the LMSC system, a final separation stage will be required to provide pure nitrogen. Either LMSC developed or alternately developed concentrator technology is applicable. One different is that oxygen/nitrogen generation would require an oxygen concentrator, rather than the normally used hydrogen concentrator.

Table VIII compares the advantages and disadvantages of these three approaches using LMSC developed technology.

Recommendations

O_2/N_2 Side Operation:

- o During the extent of N_2 generation at the cathode
- o Determine the minimum concentration of O_2 for safe operation
- o Develop inerting procedure
- o Improve electrodes
- o Determine effect of N_2H_4 concentration on a bare areas
- o High penalty low effort

H_2/N_2 Side Operation:

- o Determine highest voltage which can be used and not get O_2 under any conditions
- o Establish startup operational mode
- o Establish v, CD, N_2H_4 concentration characteristics
- o Define cathode N_2 loss
- o Improve electrode design
- o Establish control modes

Decomposer

- o Confirm NH_3 free operation
- o Develop design concept
  - single gas/liquid interface
  - single catalyst surface
  - hydrazine feed control

Table IX

SYSTEM COMPARISON

	1.5 Volts	0.1 - 1 Volt	Decomposer 0 Volts
ADVANTAGES:	o No NH_3 formation o Complete elimination of H_2 o Single step production of cabin N_2 o Could be used as a backup O_2 supply o Offers control of O_2 and N_2 in a single unit	o No NH_3 formation o Requires separation of H_2 o Requires H_2 separation o Partial H_2 separation in cell o Possible use as back-up O_2 supply	o No NH_3 formation o Requires separation of H_2 o Requires separation of H_2 o Simplified design o Lowest decomposer penalty o Complete utilization of N_2
DISADVANTAGES:	o Possible electrode failure if voltage drops o Highest system penalty due to high power requirement o Requires O_2 concentrator for pure N_2 supply o Cathode N_2 losses	o Requires H_2 concentrator for pure N_2 supply o Modest power requirement may be competitive with NH_3 producing decomposer o Unknown N_2H_4 feed control problems o Cathode N_2 losses	o Requires largest H_2 concentrator for pure N_2 supply o Unknown N_2H_4 feed-control problems
RECOMMENDATIONS:	o Keep to provide backup O_2 system o Develop improved electrode - lower volt anode - lower cathode loss	o Investigate possible operation range-likely drop	o Primary emphasis - new design including single catalyst sources new control scheme.

- o Establish safe operational procedures
  - start up
  - hydrazine limiting
  - shutdown

Conclusions

- o LMSC O_2/N_2 - highest penalty, developed technology, good backup
- o LMSC H_2/N_2 - little merit
- o LMSC Decomposer - new technology requires developments, high penalty reduction potential through use of low temperature operation and elimination of ammonia.

Section 3

CONCLUSIONS

The basic objective of this program was to investigate the electrode, cell design to improve performance, and to evaluate the elevated temperature capability of the system, and to test and evaluate the system and components fabricated in NAS 9-13051. Conclusions relating to the various parts of this report are presented below.

Electrodes

Anode - Modifications to the catalyst mixture ratios and to mixture application techniques resulted in improvements in mixture adhesion as well as providing a more homogeneous electrode covering. The mixture components and ratios are considered to be optimum. Electrical performance is slightly improved.

Cathode - Electrical performance showed substantial improvement with the addition of carbon black to and the modification of the mixture ratios. The new mixture also showed considerable improvement in the areas of adhesion and homogeneity. It was finally concluded, however, that the anode formulation could also be used for the cathode. This trades off a slight loss in hydrazine efficiency for an improvement in electrical performance. There is also the added benefit of making only one kind of electrode.

Membranes - The overall conclusion is that the membranes should be non-metallic and that PVC (polyvinyl chloride) as formulated for battery separators is satisfactory. It is chemically compatible in the long term and has adequate mechanical strength. Its drawbacks are relatively low

bubble point and poor quality control (in battery separator form). The membrane area could benefit from additional investigation.

Asbestos - The problem of a source for the Acco asbestos was not resolved. This area needs further investigation.

Molded Cell Spacers - Once a proper annealing technique was devised, the molded cell spacers proved satisfactory in design and material.

Cell Stack - The cell stack concept and design is considered satisfactory, especially in light of its much improved ease of assembly. This improvement is due largely to slurrying the asbestos onto the membrane rather than onto the electrode.

Pump/Bubble Separator - As a result of minor redesign and the substitution of stainless steel parts for polysulfone parts, the P/BS is now suitable for operation with electrolyte temperatures up to about 71°C (160°F).

Heat Exchanger - it is concluded that the heat exchanger in the electrolyte loop should be all plastic; however, if metallic materials are considered all electrolyte passages must be thoroughly coated with plastic.

Nitrogen/Oxygen Production - Problems encountered in attempting to electrolyze hydrazine in the engineering prototype system have made it questionable whether this system design could be satisfactorily used as a source of mixed nitrogen and oxygen in the electrolysis mode. Further, the question of whether the system could be efficiently used for the catalytic decomposition of hydrazine was unresolved. If serious consideration is given to either of the above uses, further investigation is, without question, necessary.

REFERENCES

1. B. M. Greenough, "The Development and Preliminary Design of an Oxygen/Nitrogen Generation System", CR 66940, NAS1-7706, June 18, 1970.

2. B. M. Greenough, "The Development of a Non-Cryogenic Nitrogen/Oxygen Supply Technique", CR 114912, NAS 9-10405, 17 May 1971.

3. B. M. Greenough, R. E. Mahan, "Development of a Non-Cryogenic Nitrogen/Oxygen Supply System", LMSC-D401948, NAS 9-13051, June 1974.

Library Card Abstract

An investigation was conducted to refine and test an engineering demonstration type hydrazine/water electrolysis system designed and fabricated in a previous contract. The design is applicable to manned spacecraft requiring metabolic oxygen and both oxygen and nitrogen for cabin leakage make-up. The improvement in and test evaluation of the module performance was limited due to problems encountered with gassing in the cell, materials compatibility with hydrazine and various components. Major interest centered on the cell design and the gassing problem encountered within the cells. Electrode and phase separation design received primary attention. Also a trade study was made of various means of providing oxygen and nitrogen to a spacecraft. The study includes ways the circulating electrolyte type electrolysis system might be used to provide nitrogen with essentially the same hardware design as normally would be used to provide a mixture of nitrogen and oxygen.

Appendix A

ANOMALOUS BEHAVIOR OF METALLIC, GAS-LIQUID SEPARATOR SCREEN IN WATER ELECTROLYSIS SYSTEM

1.0 INTRODUCTION

In the LMSC water-electrolysis system, a gas-liquid separator screen is placed on the liquid side of each gas-evolving electrode. The screen presses a wetted asbestos pad against the electrode while the holes in the screen are small enough (ca. 5 microns) to prevent gas from passing through the screen to the bulk electrolyte at reasonable pressure differences (ca. 36" H_2O head). The screen thus serves as a gas-liquid separator keeping the bulk electrolyte free of gas even though both product gases are regulated to a pressure higher than the electrolyte.

Since this gas-liquid separating screen is metallic, two conditions may arise which could result in the anomalous electrolysis behavior observed in the system:

- o complete blockage of separator pores during electrolysis by gas forced through the asbestos because of excessive gas over liquid pressure build-up.
- o electrical current flow in the screen matrix through high impedance paths.

The former condition results when gas pressure difference across the electrode assembly becomes sufficiently large, e.g., about 50" H_2O head, so that gas passes through the asbestos but not quite through the separator membrane. However, gas may be forced into the separator pores, and the impressed current may then pass through the screen rather than through the electrolyte which would normally fill the pores of the screen, as indicated in Figure 1. For current densities larger than a few mA/cm^2, the metallic screen may then become a bipolar electrode because it is not physically touching the electrode assembly proper. Hence the physical

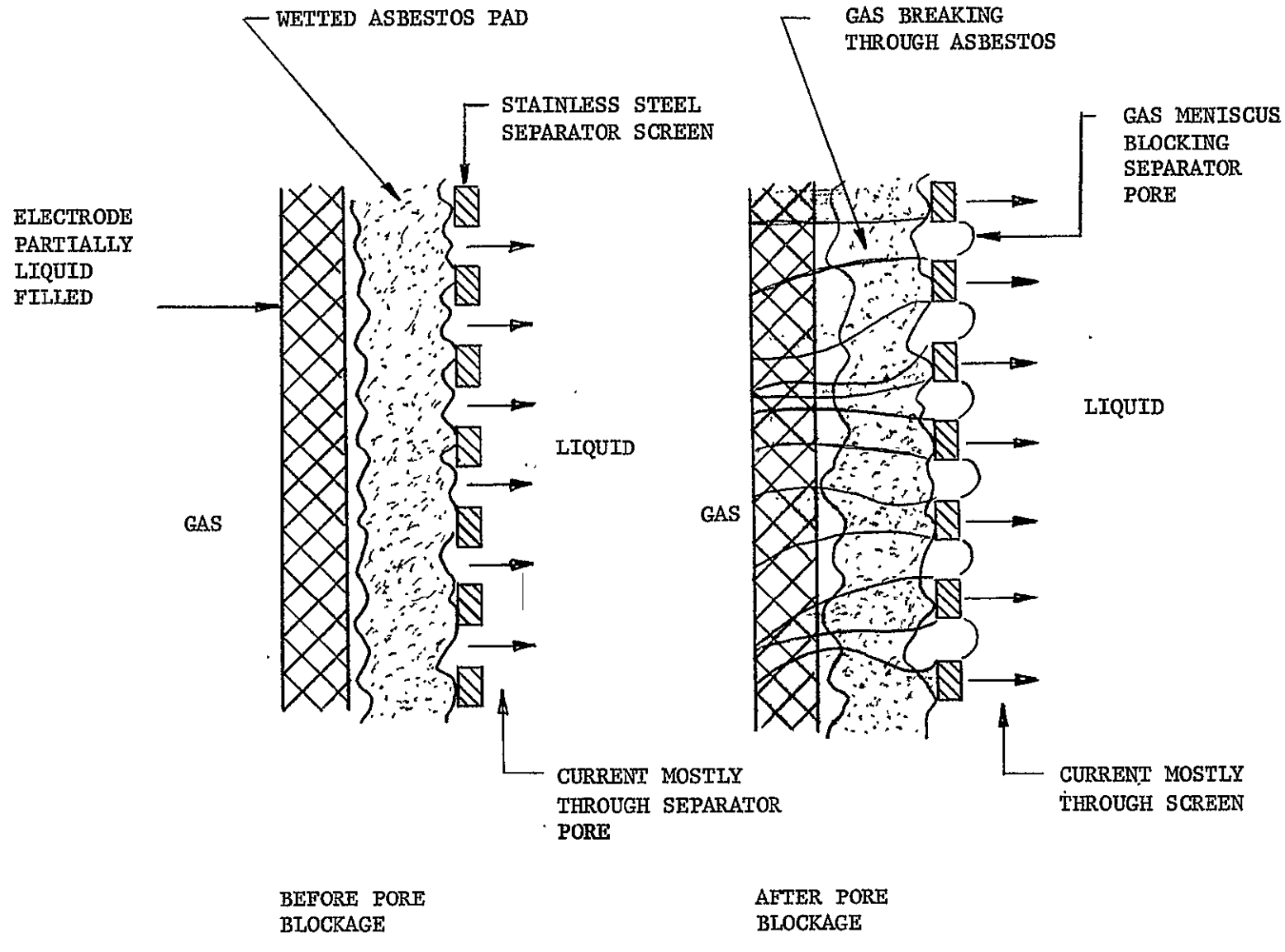


Figure 1 Diagram Showing Mode of Pore Blockage (to Current) When ΔP Is Excessively High

separation of the electrode and the metal membrane may allow the generation of hydrogen and oxygen on opposite sides of each screen at the same time. Thus gas formation may occur in both the asbestos pad and bulk-electrolyte regions. However, during this process portions of the asbestos pad must remain wetted with the electrolyte to provide electrical paths to the separator, otherwise no current would flow.

The screen with its pore matrix incompletely flooded with electrolyte, may have high ohmic resistance, and with a constant current controlled power supply a difference of over 1.23 volts across this matrix could occur and consequently cause water electrolysis. This is the second condition noted above.

2.0 PROBLEM STATEMENT

During operation of the water-electrolysis system, gas has been observed in bulk electrolyte apparently under conditions where neither high pressure differences exist nor high electrical impedances are formed in the separator screen. The presence of gas in the bulk electrolyte creates difficulties in operating the electrolyzer, and experiments reported here are an effort to eliminate this gas intrusion by understanding its basic causes.

3.0 TECHNICAL APPROACH

An electrical current is passed through a stainless steel separator screen immersed in 7.0 M KOH electrolyte, in a cell as indicated in Figure 2. Both sides of the screen and the electrolyte are observed during passage of a typical current density, about 150 mA/cm^2, for evidence of gas evolution, and the ohmic resistance through the separator screen is measured both before and after current passage for 3 - 5 hours.

The cell was 3.0 cm in dia. and 6.0 cm long, with the screen being midway between two platinum electrodes, 3.0 cm in dia., placed at both ends of the cell. The cell was constructed from Lucite so that visibility could be maintained.

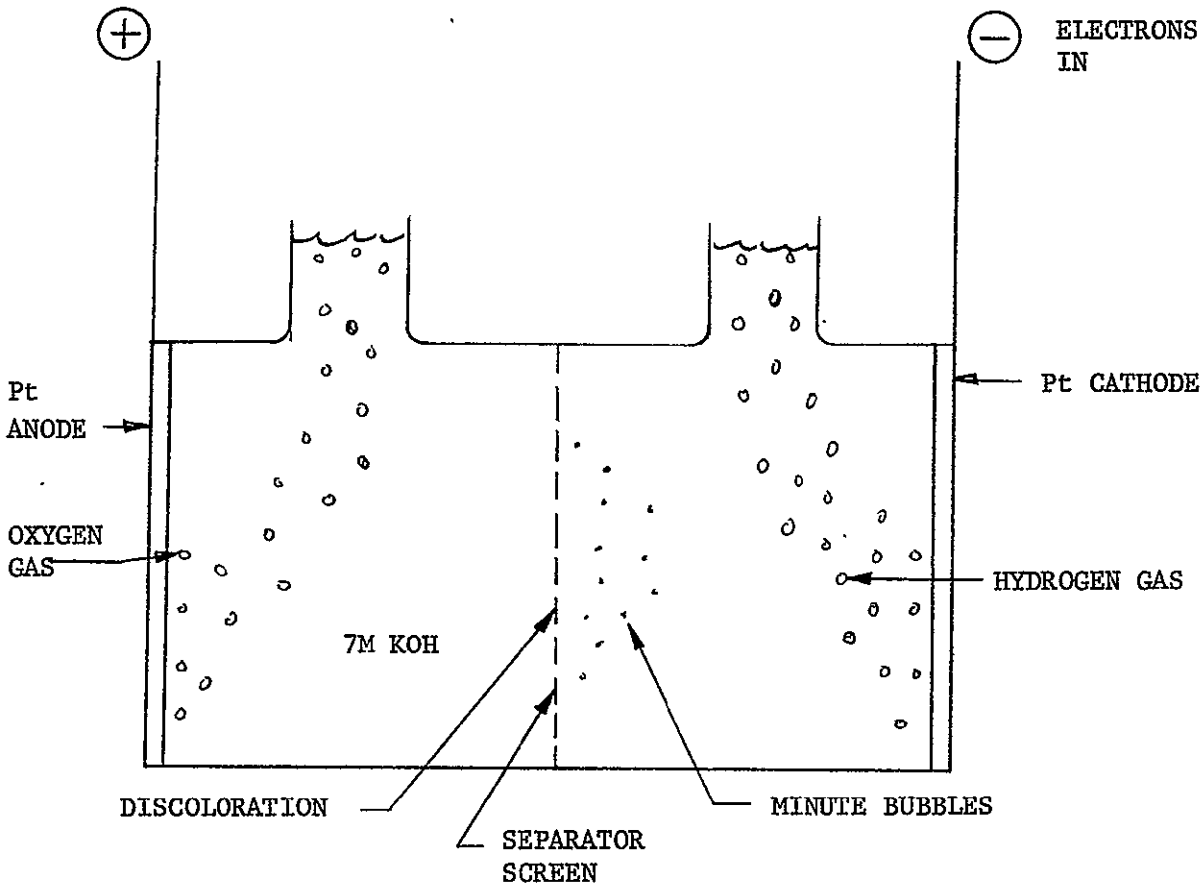


Figure 2 Diagram of Experimental Cell

The stainless steel separator screen was fastened with epoxy between two thin Lucite plates, with 0.60 cm dia. in each plate to expose only a 0.60 cm circle for a current path through the screen. Constant current was applied with an Electronic Measurement Model C 612 galvanostat, resistance was measured with a General Radio Co. Impedance Bridge Model 1650 A (at 1 KC), A Greibach Model 500 Ammeter was used to measure current, and a Sarkes direct current voltmeter was used to measure cell voltage.

4.0 RESULTS AND DISCUSSION

Ohmic resistance was typically 4.5 ± 0.5 ohms*, remaining unchanged when measured before and immediately after current passage for 3 - 5 hours at 120 or 370 mA/cm^2. This invariance, before and after cell operation, demonstrates that no irreversible change occurred in the screen separator resistance which could influence the overall current passage under the conditions of the experiment. Also, at the applied constant current, the cell voltage remained constant at 2.1 volts, again indicating no large, gradual change in the screen's impedance under the conditions of the experiment, e.g., at 120 mA/cm^2 which is a typical current density for the electrolyzer.

When the screen separator was removed from the cell, the ohmic resistance through the electrolyte was the same as it was through the electrolyte with the screen present. The portion of the resistance due to the screen is thus considered negligible compared to the 4.5 ohms measured through the cell. The voltage change across the electrolyte and screen for the 34 mA of applied current (120 mA/cm^2 on 0.6 cm circle) would only be $0.034 \times 4.5 = 0.15$ volts for a primary current distribution, not enough to cause electrolysis at the screen. According to these measurements, high impedances do not appear to be formed in current paths across the separator screen. The observed cell voltage, 2.0 - 2.1 v, can be accounted for by 1.23 v needed for electrolysis and about 0.8 v polarization.

*For 7M KOH, = 2 ohm-cm, and the measured resistance should theoretically be about 2 ohm. This is in reasonable agreement with 4.5 ohm (measured) considering varying geometrical factors of the cell.

During cell operation (current passage at 120 mA/cm^2), small bubbles were observed to form at and leave the side of the screen which faced the hydrogen evolving platinum electrode, and no bubbles were observed leaving the opposite side. The bubbles from the cathode side of the screen were evolved at an estimated rate of some 1/1000 the rate of hydrogen evolution from the platinum cathode.

Minute bubbles were also found to nucleate throughout the system forming on the Lucite and gradually growing in size from the accumulation and agglomoration of smaller bubbles from the platinum anode and cathode on the respective sides. These bubbles were not confused with bubbles which appeared to actually emanate from the screen.

After disassembly of the cell after 3 - 5 hrs. of current passage, the side of the screen facing the oxygen-evolving platinum electrode was discolored while the cathode side was not changed in appearance. This sense of discoloration is also corroborated by observations of the disassemblied full-scale pilot electrolyzer.

An adequate explanation for the observations above, for the minute gas evolution and discoloration, has not been formulated. It appears as though the screen is becoming a bi-electrode, with anodic oxidation on the platinum anode side and hydrogen evolution on the platinum cathode side, in an opposite sense to the traditionally anticipated one. Such gas evolution, however, could explain gas instrusion into bulk electrolyte if the pressure difference across the separator is approaching the break-through pressure. A small disturbance, such as electrochemical gas evolution, could initiate a gas break-through (bubbling), and the normal hysteresis in the flow pressure curve would require much lower pressures to restore the gas balance at the separator.

When the current density was increased to 270 mA/cm^2 the effects noted above were not observed. Also, when the area of the screen was increased to 3.0 cm dia., the discoloration was not so marked, although there was still evidence of bubbles at the platinum cathode side.

5.0 SUMMARY AND CONCLUSIONS

Preliminary experiments have indicated that minute bubbling can occur at stainless steel screens used as gas/liquid separators when the screens are immersed in 7 M KOH with a current of 120 mA/cm^2 passed through them. The bubbles appear at about 1/1000 the coulombic rate of the passed current at the side of the screen facing the cathode (H_2 evolution). The opposite side of the screen is discolored.

It is anticipated that the minute bubbles can cause gas break-through, provided the pressure difference is near the break-through pressure range.

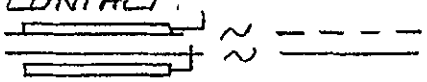
Appendix B

SMALL SCALE ANODE AND CATHODE VOLTAGE SWEEP DATA

ELECTRODE SCREENING

VOLTAGE/CURRENT PROFILE

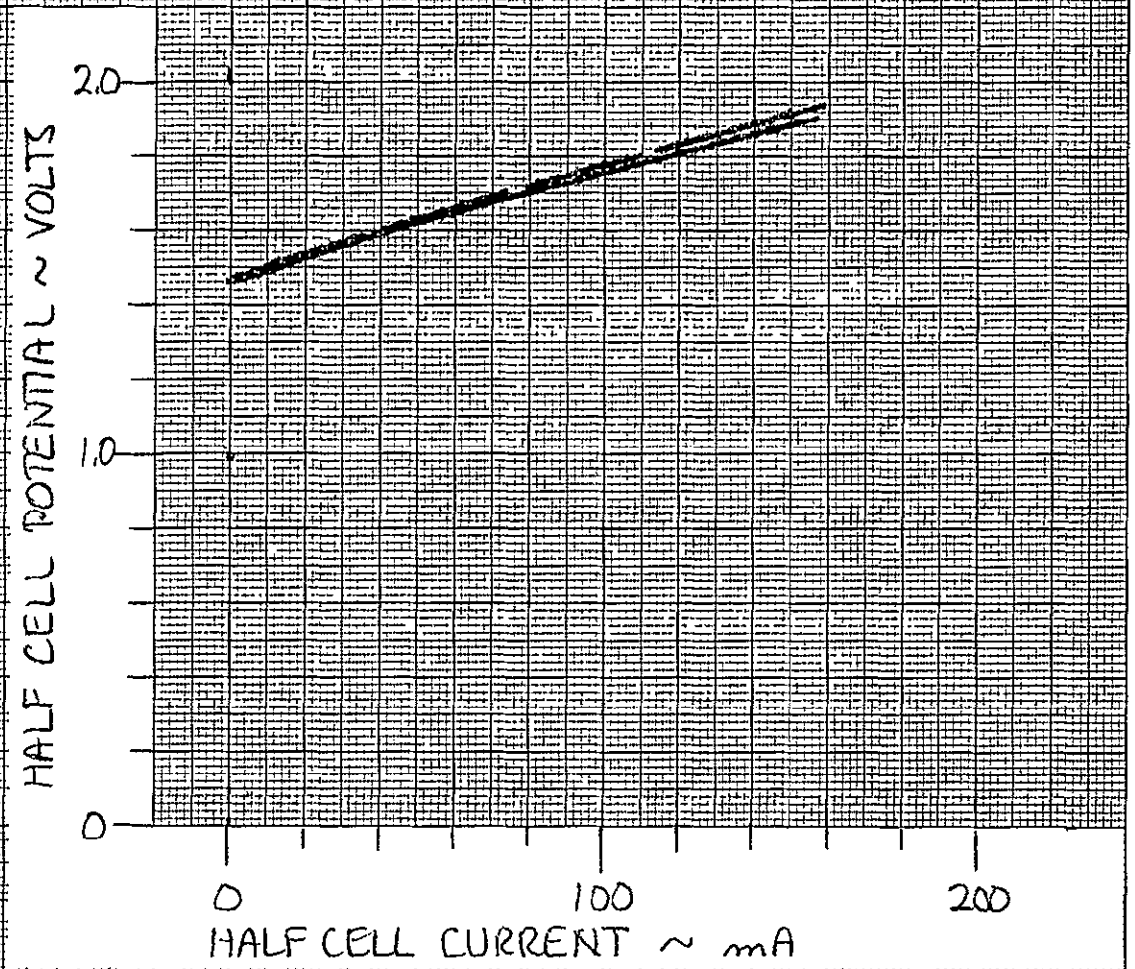
SAMPLE # 1A: ANODE ELECTRODE/ELECTROLYTE CONTACT:



SAMPLE AREA: 1 CM^2

SWEEP RATE: 30V/HR

17 JULY 74



ELECTRODE SCREENING

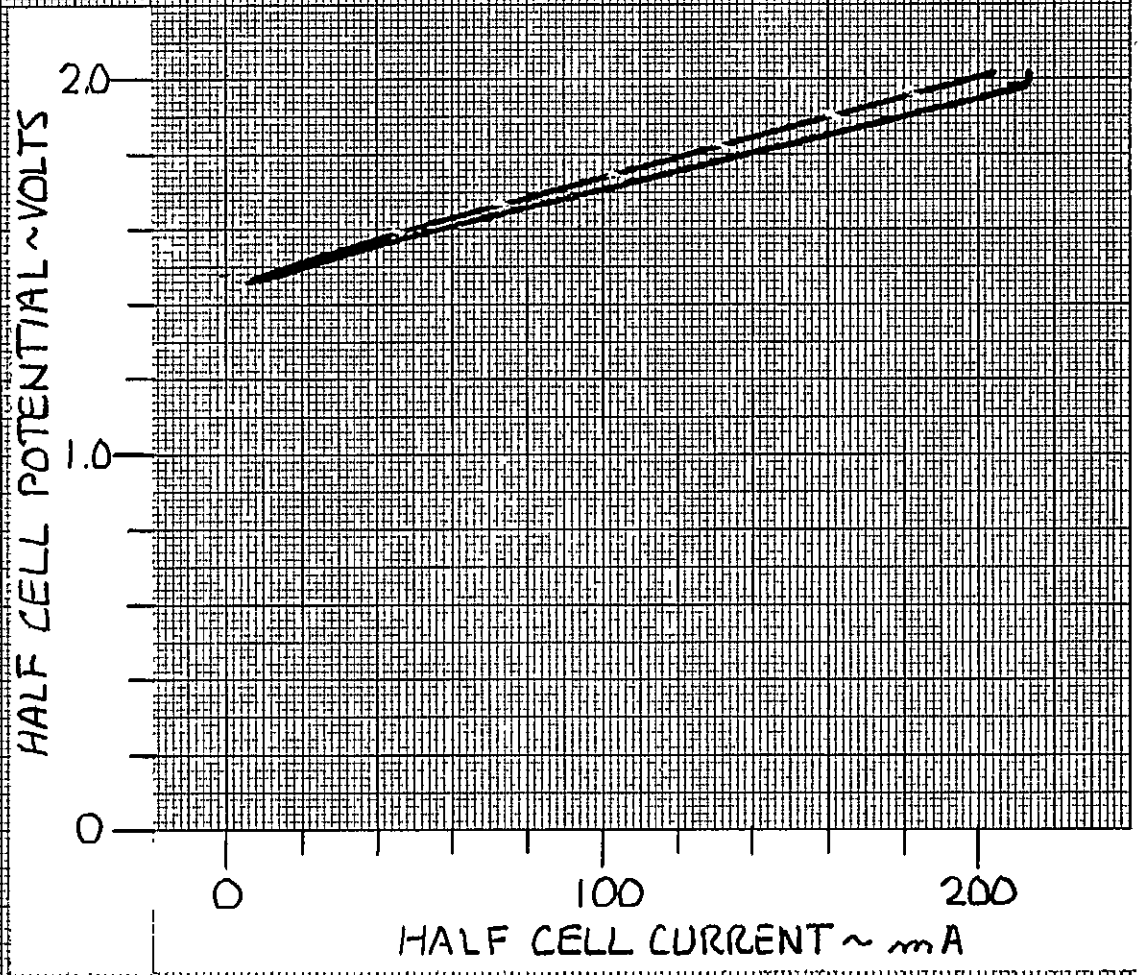
VOLTAGE / CURRENT PROFILE

SAMPLE #2: ANODE ELECTRODE/ELECTROLYTE CONTACT:

SAMPLE AREA: 1 CM^2

SWEEP RATE: 30 V/HR

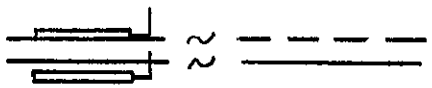
14 JUNE 1974



ELECTRODE
SCREENING,
VOLTAGE/CURRENT
PROFILE
SAMPLE #3: ANODE
ELECTRODE ELECTROLYTE
CONTACT:
SAMPLE AREA: 1 CM²
SWEEP RATE: 30 V/HR
14 JUNE 1974
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

ELECTRODE SCREENING, VOLTAGE/CURRENT PROFILE

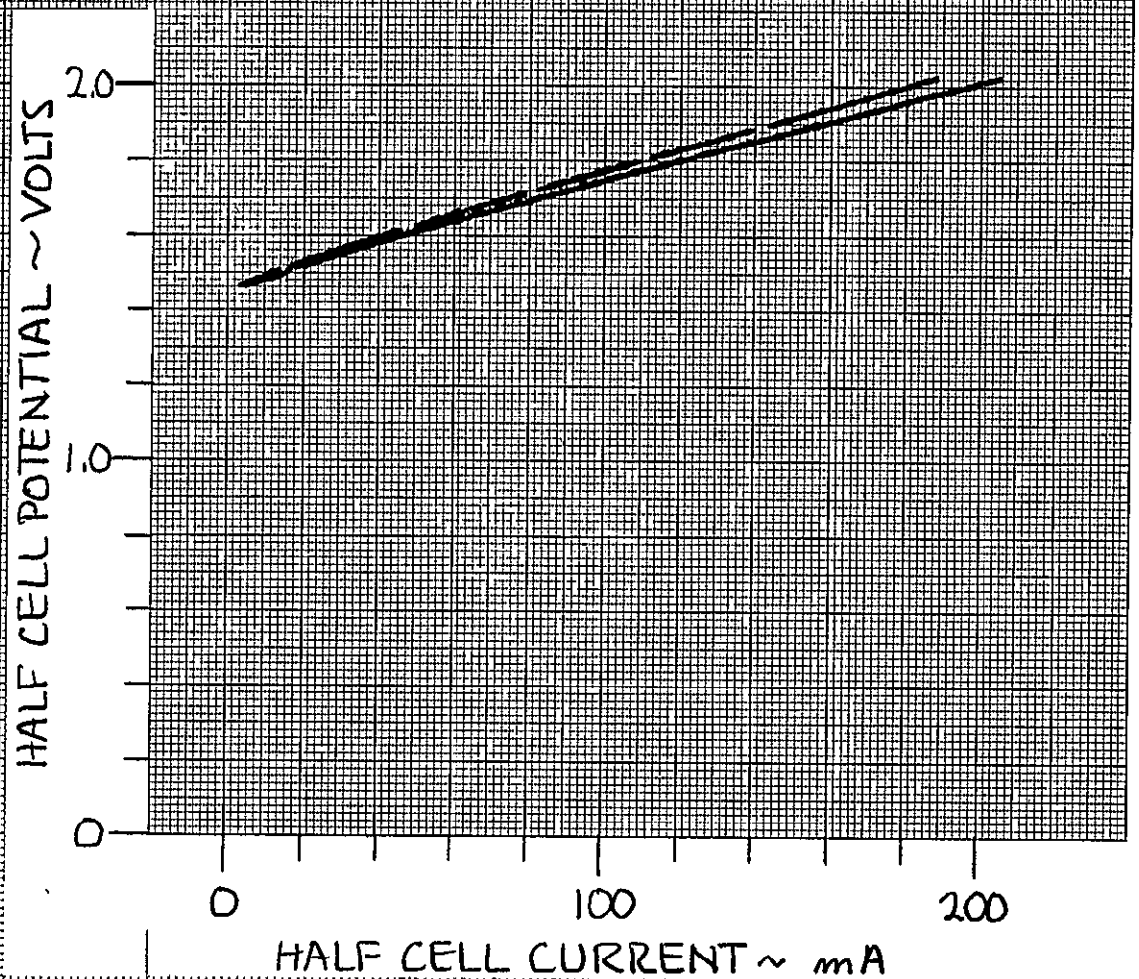
SAMPLE #4: ANODE ELECTRODE ELECTROLYTE CONTACT:



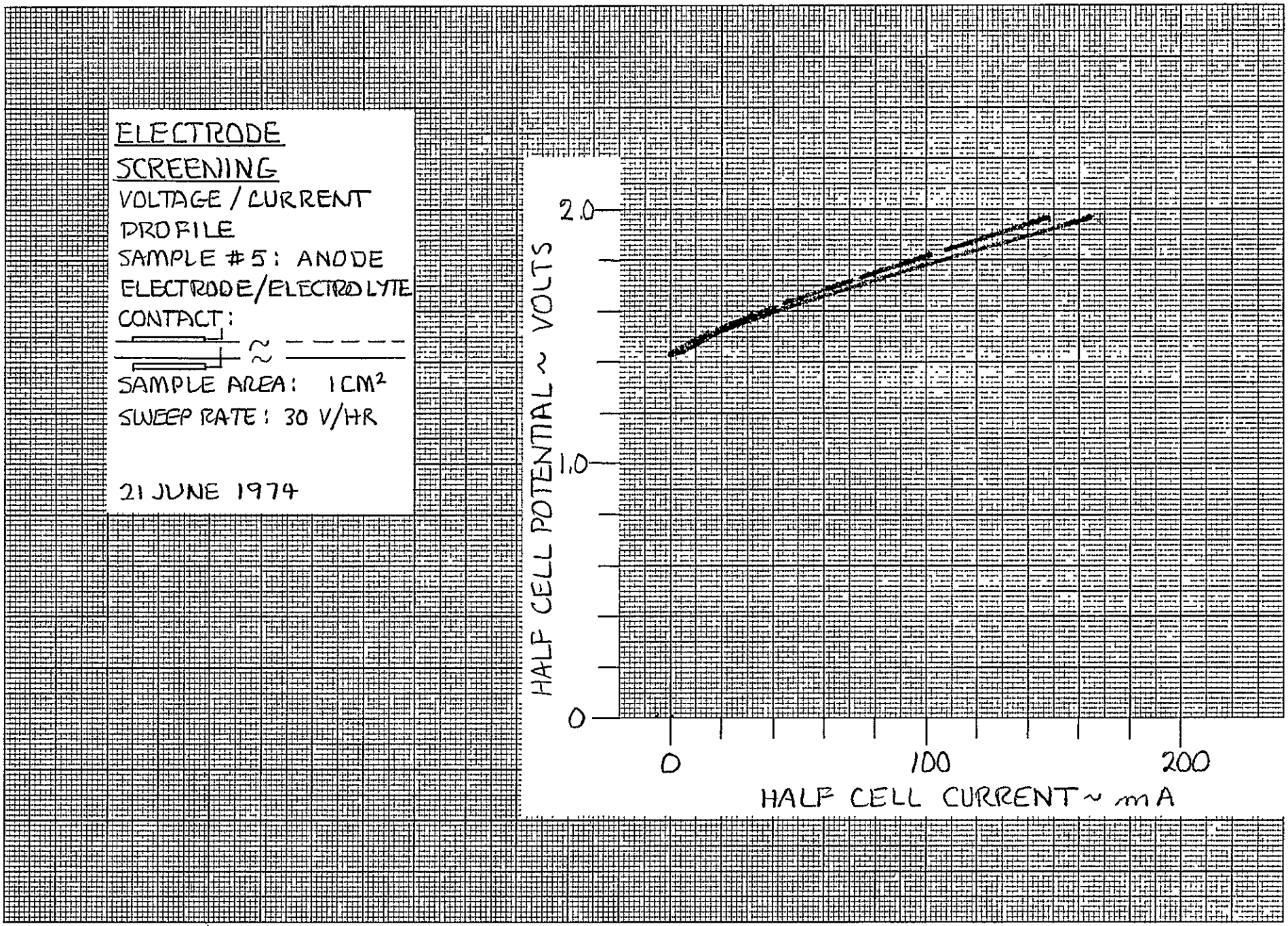
SAMPLE AREA: 1 CM^2

SWEEP RATE: 30 V/HR

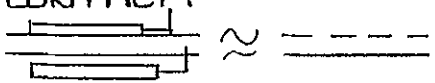
14 JUNE 1974



A-2

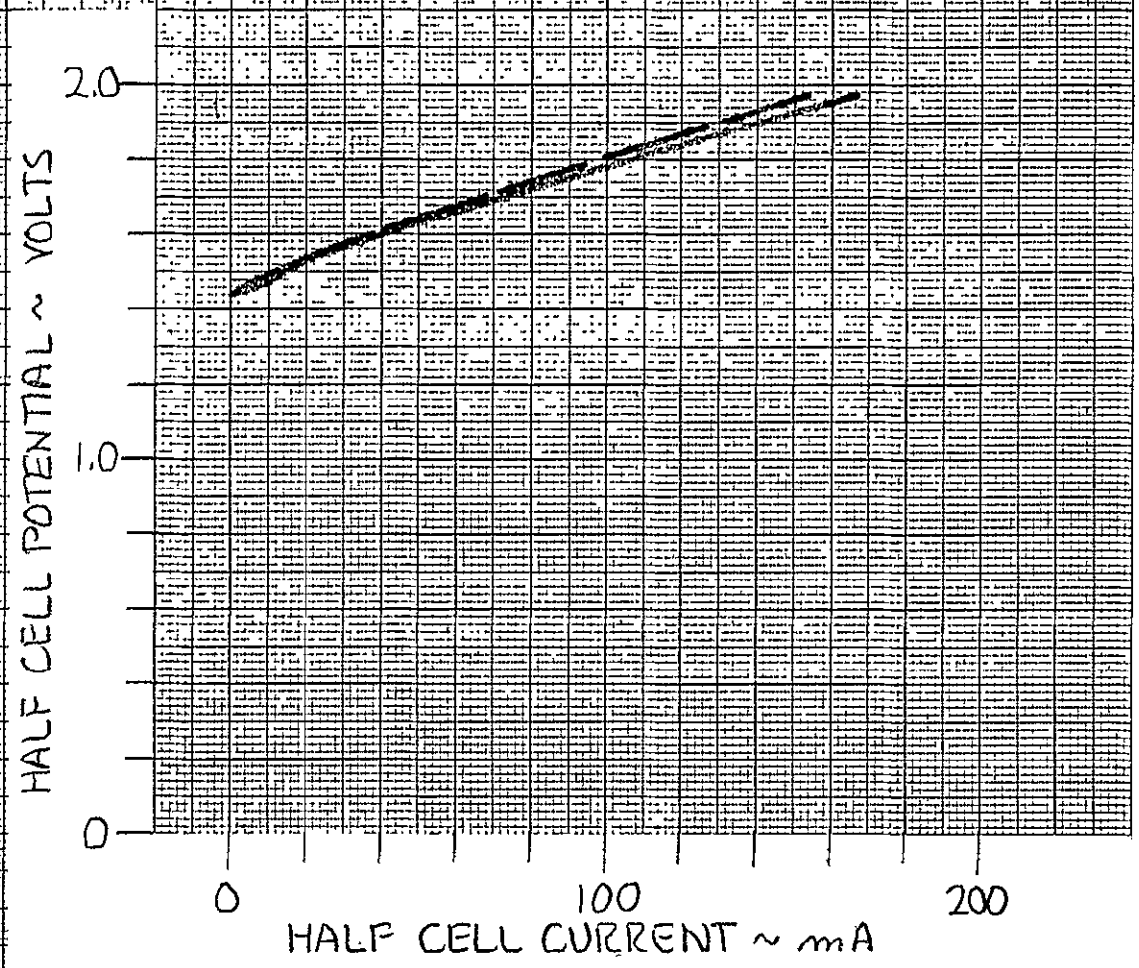

ELECTRODE SCREENING
VOLTAGE / CURRENT PROFILE
SAMPLE #5: ANODE
ELECTRODE/ELECTROLYTE CONTACT:
SAMPLE AREA: 1 CM²
SWEEP RATE: 30 V/HR
21 JUNE 1974
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

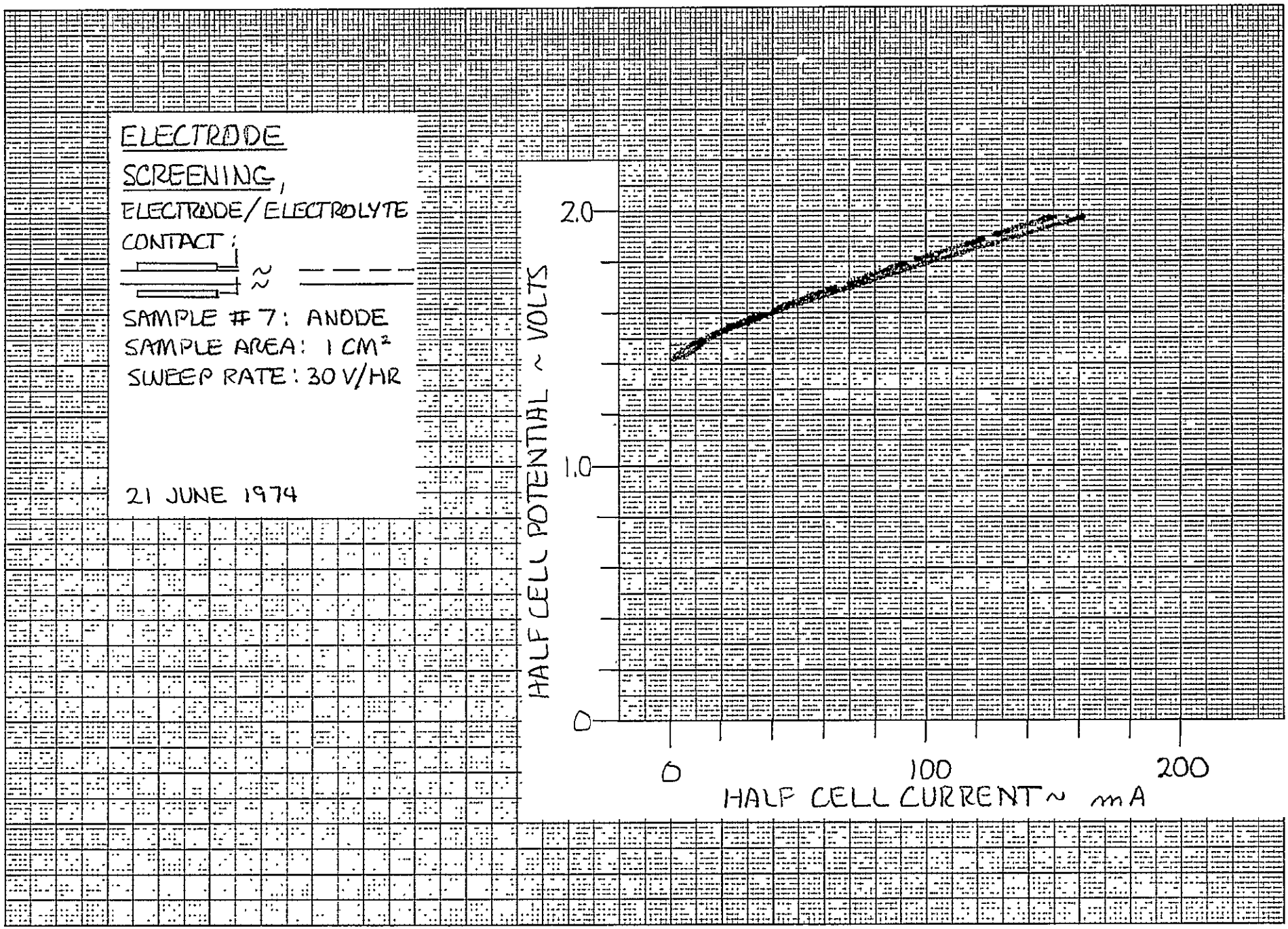
ELECTRODE SCREENING,
VOLTAGE / CURRENT PROFILE
SAMPLE #6 : ANODE
ELECTRODE ELECTROLYTE
CONTACT :



SAMPLE AREA: 1 CM^2
SWEEP RATE : 30 V/HR.

21 JUNE 1974



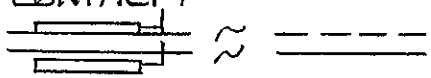

ELECTRODE
SCREENING,
ELECTRODE/ELECTROLYTE
CONTACT:
SAMPLE #7: ANODE
SAMPLE AREA: 1 CM²
SWEEP RATE: 30 V/HR
21 JUNE 1974
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

ELECTRODE SCREENING,

VOLTAGE/CURRENT PROFILE

SAMPLE # 8 : ANODE

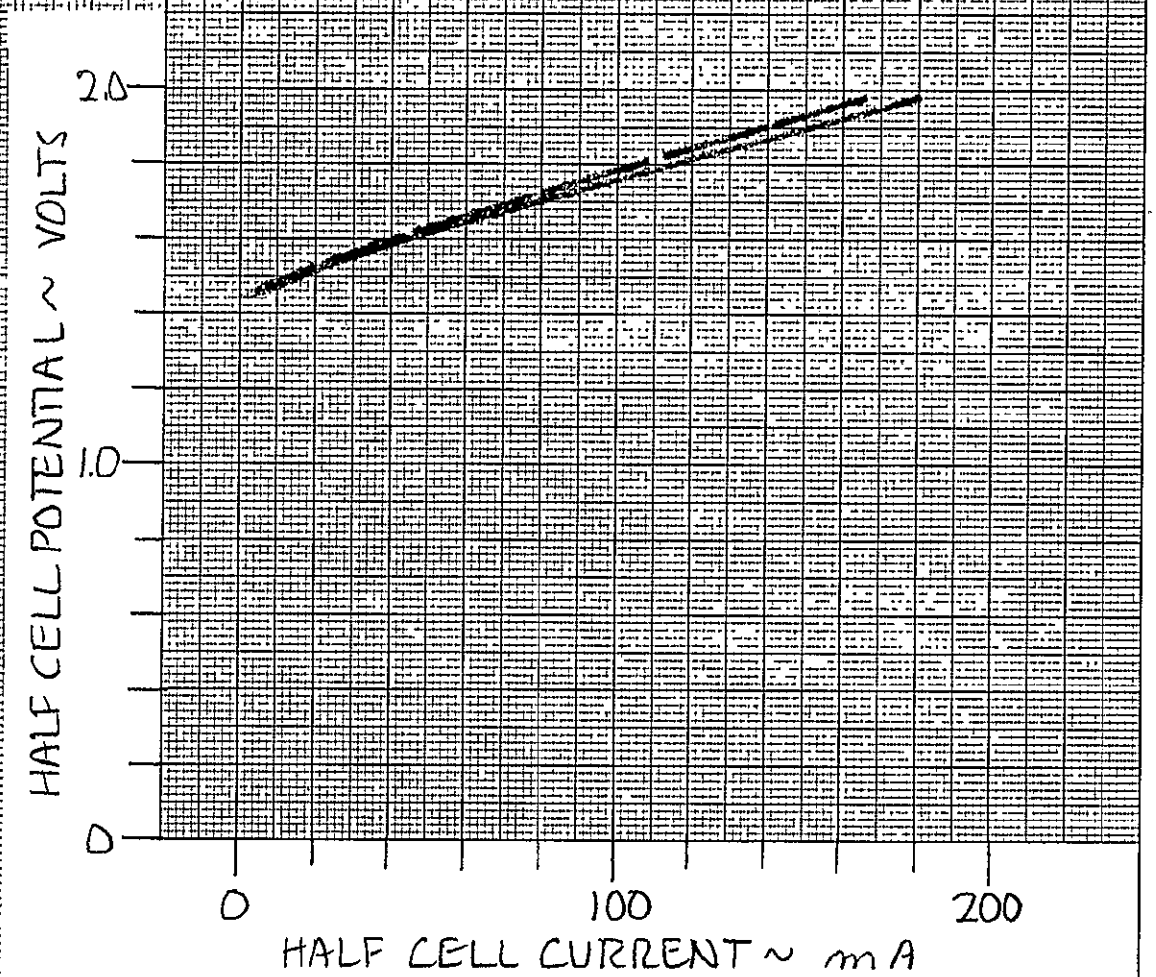
ELECTRODE/ELECTROLYTE CONTACT:



SAMPLE AREA: $1 CM^2$

SWEEP RATE: 30V/HR

21 JUNE 1974

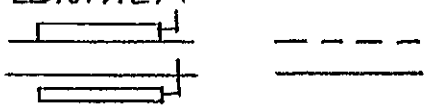


ELECTRODE SCREENING.

VOLTAGE / CURRENT PROFILE

SAMPLE #22 : ANODE

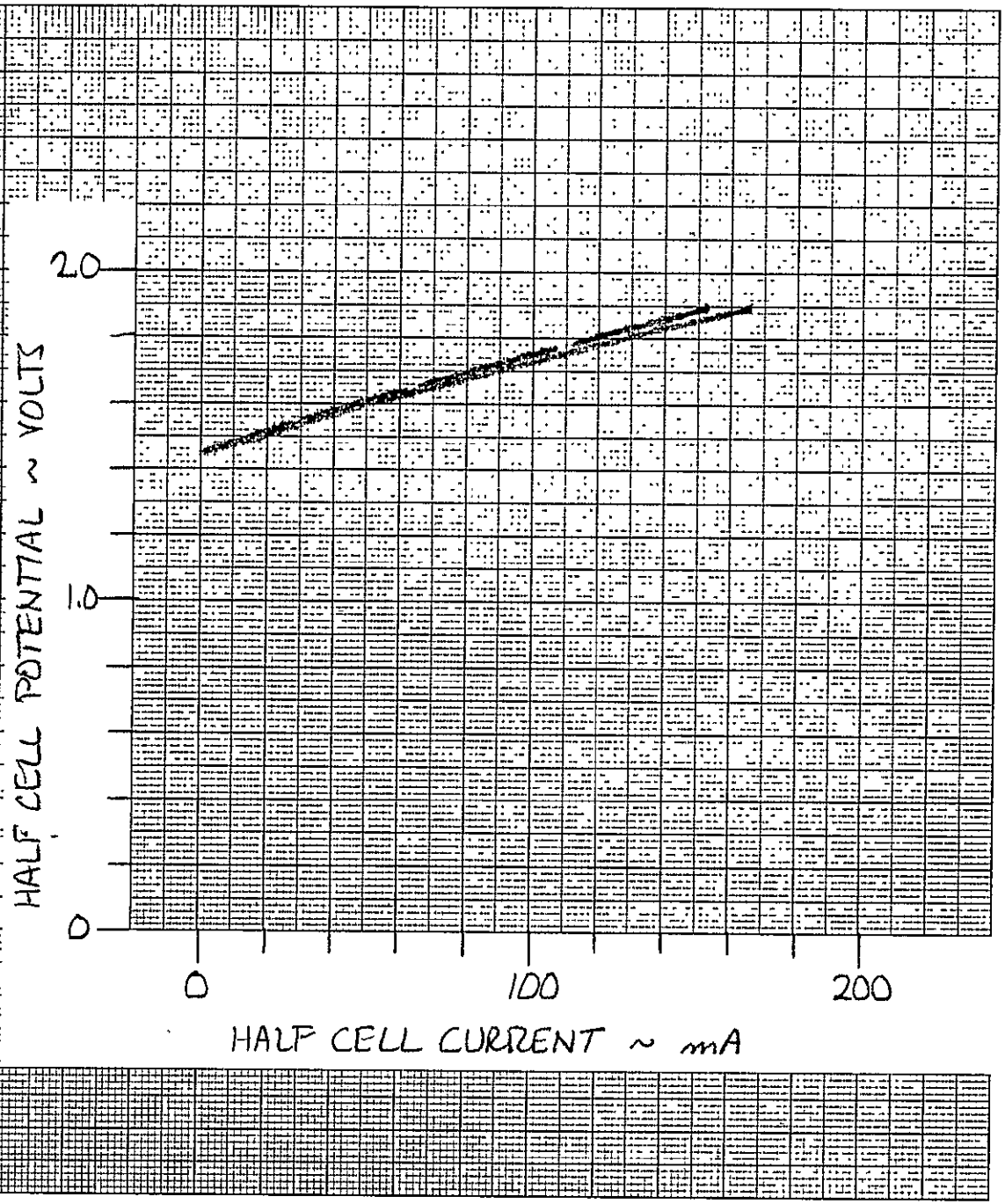
ELECTRODE / ELECTROLYTE CONTACT:



SAMPLE AREA : 1 CM²

SWEEP RATE : 30 V/HR

16 JULY '74



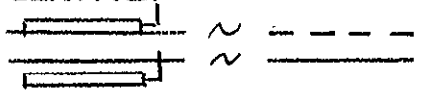
ELECTRODE
SCREENING
VOLTAGE/CURRENT
PROFILE
SAMPLE #22A: ANODE
ELECTRODE/ELECTROLYTE
CONTACT:
SAMPLE AREA: 1CM²
SWEEP RATE: 30V/HR
17 JULY 74
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

ELECTRODE SCREENING

VOLTAGE/CURRENT PROFILE

SAMPLE #23: ANODE

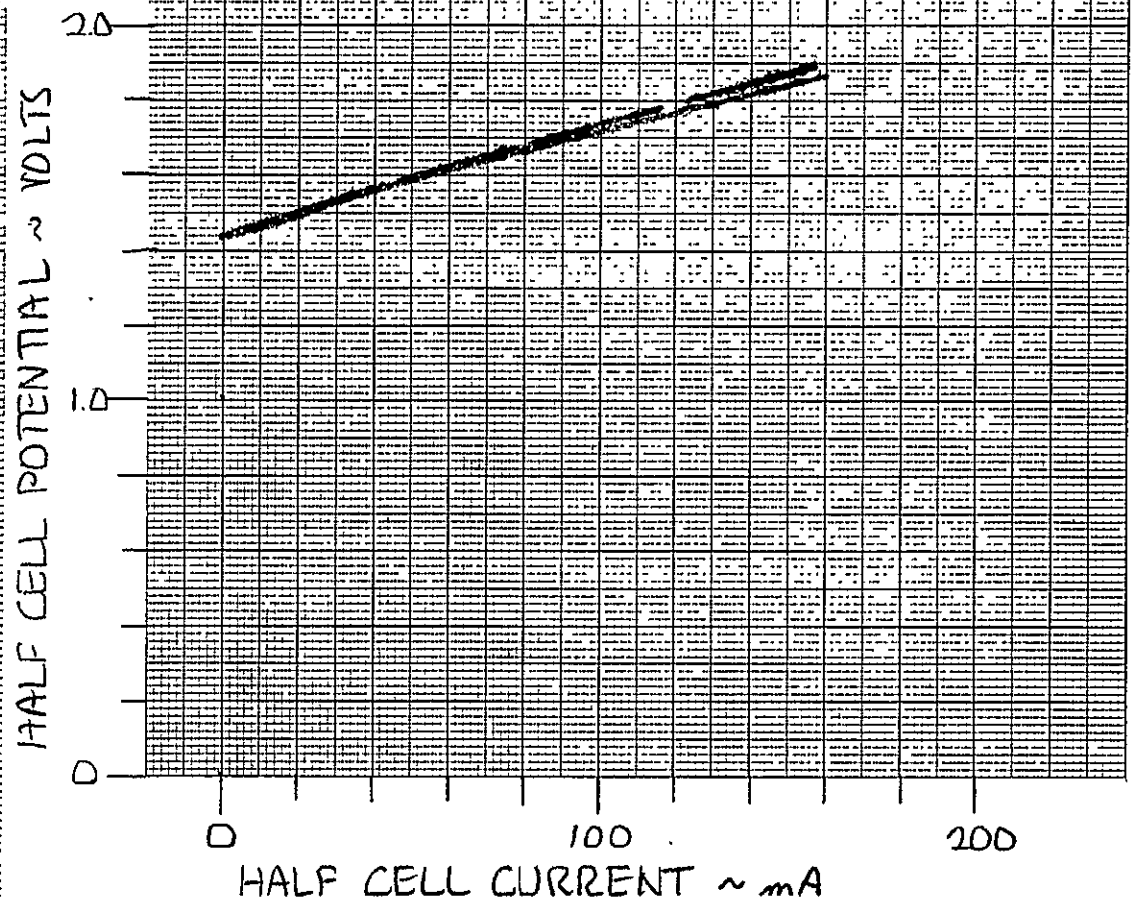
ELECTRODE/ELECTROLYTE CONTACT:



SAMPLE AREA: 1 CM²

SWEEP RATE ~ 30V/HR

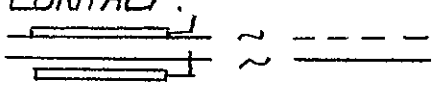
16 JULY '74



ELECTRODE SCREENING

VOLTAGE / CURRENT PROFILE

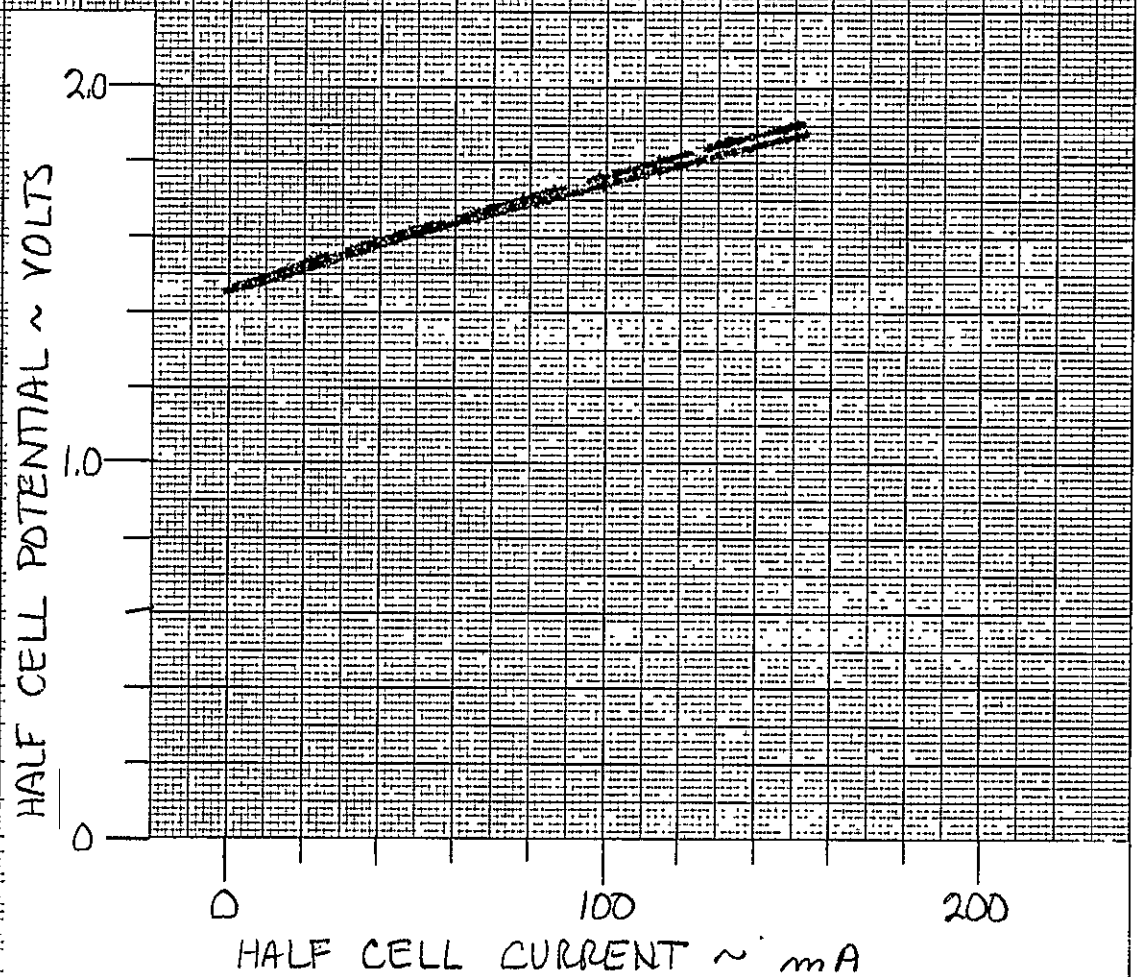
SAMPLE #23A: ANODE ELECTRODE/ELECTROLYTE COINTACT:

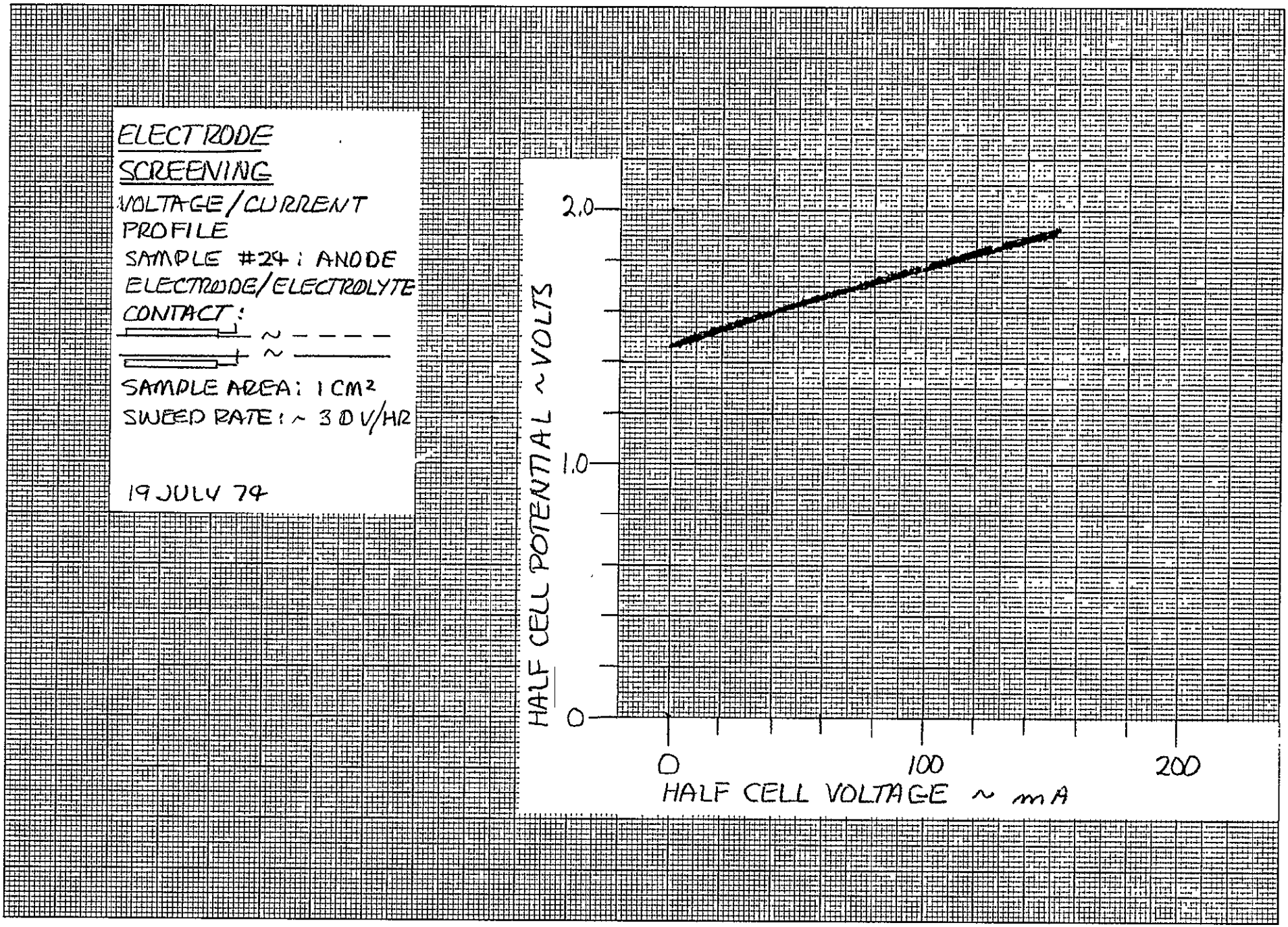


SAMPLE AREA: 1 CM²

SWEEP RATE: 30 V/HR

17 JULY 74




ELECTRODE
SCREENING
VOLTAGE/CURRENT
PROFILE
SAMPLE #24: ANODE
ELECTRODE/ELECTROLYTE
CONTACT:
SAMPLE AREA: 1 CM²
SWEEP RATE: ~ 30 V/HR
19 JULY 74
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL VOLTAGE ~ mA

ELECTRODE SCREENING
VOLTAGE/CURRENT PROFILE
SAMPLE #24A: ANODE ELECTRODE/ELECTROLYTE CONTACT
SAMPLE AREA: 1 CM²
SWEEP RATE: 30 V/HR
19 JULY 74
HALF CELL POTENTIAL ~ VOLTS
2.0
1.0
0
0
100
200
HALF CELL CURRENT ~ mA

FIG. 16

Operator _____ Sheet _____ of _____ Cell No. 10 cell module

7 February 1977

Anodes as cathodes
Anodes as anodes
#1 cell next to base plate

Time	Curr.	Voltage Cell 1	2	3	Flow Rate 4	5	6	Gas Analysis 7	8	9	10	TOT	Temp °F
0825*													
0940	10A	1.66	1.64	1.63	1.65	1.66	1.65	1.67	1.66	1.67	1.68	16.66	86
0950	20A	1.86	1.82	1.82	1.84	1.86	1.86	1.90	1.87	1.89	1.90	18.62	88
0955	21.75	1.88	1.84	1.84	1.87	1.90	1.88	1.92	1.90	1.92	1.93	18.93	91
1015	"	1.81	1.77	1.76	1.79	1.82	1.81	1.83	1.82	1.84	1.84	18.16	117
1018		5 second water feed (manual)											
1030	21.75	1.75	1.73	1.72	1.75	1.77	1.77	1.78	1.78	1.80	1.80	17.71	131
1040	21.75	1.74	1.71	1.71	1.73	1.75	1.75	1.77	1.76	1.77	1.79	17.51	135
1053	21.75	1.73	1.72	1.70	1.73	1.74	1.74	1.75	1.75	1.77	1.78	17.43	140
1112		5 second water feed (manual)											
1121	21.75	1.72	1.70	1.69	1.72	1.72	1.73	1.74	1.74	1.76	1.75	17.29	145
1240	21.75	1.71	1.71	1.69	1.72	1.73	1.73	1.74	1.74	1.75	1.76	17.33	144
1300	21.75	1.71	1.69	1.69	1.70	1.71	1.72	1.73	1.72	1.74	1.75	17.19	149
1310		5 second water feed (manual)											
1325	21.75	1.71	1.70	1.69	1.70	1.72	1.72	1.73	1.72	1.74	1.75	17.20	149
1410		1.71	1.70	1.69	1.72	1.74	1.74	1.75	1.74	1.76	1.75	17.33	144
1450	0	shutdown - power supply hot											

*Startup circulation only (there is interference in the P/BS) the reservoir does not appear to be fuctioning properly - as though the bellofram is stuck or folded. Manual waterfeed gets norise in volume indication, both purge solenoids are steady open (system purged over the weekend) P/BS not dumping gas either "wheel" is stuck or sensor is malfunctioning - valve is woking ok in manual.

Appendix D
Process Specification

Catalyst Preparation & Application

1. Scope This specification establishes the requirements for the preparation and application of catalyst material to the electrodes used in the O_2/N_2 prototype module (NAS 9-13720).

2. Applicable Documents

Lockheed	
LMSC-D401948	The Development of a Non-Cryogenic Nitrogen/Oxygen Supply System

3. Requirements

3.1 Materials and Equipment

3.1.1 Materials. Materials used in this process are:

1. Platinum black, catalytic grade
2. Iridium black, catalytic grade
3. Carbon black 50% comp.
4. Binder (DuPont TFE coating 852-201)
5. Extender (Trade name "Jaguar")
6. Potassium Hydroxide in water (30%)
7. Hydrochloric acid (10%)
8. Isopropyl Alcohol
9. Distilled water
10. Polyester Film (.005-.010 thick)

3.1.2 Equipment

1. Precision balance
2. Liquid containers (stainless steel or glass) of sufficient size to completely immerse an electrode support screen.
3. Laboratory hot plate (1000 watts min.)
4. Ultrasonic shaker for use with 2.
5. Catalyst rolling fixture
6. Temperature controlled oven

3.2 Process Procedure

3.2.1 Catalyst Preparation. The catalyst mixture components shall be accurately weighed in accordance with final report for NAS 9-13720 and mixed until a cohesive, chewing-gum like mass is achieved. This mass shall be rolled to a thickness of approximately .01 inches and cut in half.

3.3 Catalyst Application. The two halves of the rolled catalyst mixture shall be applied to both sides of the electrode support screen and placed between two layers of polyester film. The assembly shall be rolled (from both sides) until the catalyst mixture is worked completely through the and encapsulates the support screen. The polyester film is then removed.

3.4 Catalyst Leaching. The completed catalyst/support screen assembly shall be leached in accordance with Table 6 of LMSC-D401948.

3.5 Drying. The leached assembly shall be dried in an oven for no less than four hours at no more than $38^{o}C(100^{o}F)$.

4. Quality Assurance Provisions

4.1 Test Methods

4.1.1 Materials Inspection. Materials inspection shall consist of verification that all materials are in accordance with applicable specifications.

4.1.2 Visual Inspection. The dried catalyst mixture shall be visually inspected for uniformity of thickness and surface texture, completeness of coverage and adhesion to the support screen.

4.1.3 Residual Extender Inspection. Scrapings from each dry support screen assembly shall be subjected to thermogravinometric analysis (TGA) to determine the amount of residual extender. Residual extender shall not exceed 1%.

5. Notes

5.1 Intended Use. This process specification is intended for use in catalyst preparation and application as related to the O_2/N_2 prototype module (NAS 9-13720).

Appendix E

Process Specification

Asbestos Preparation and Slurrying

1. Scope. This specification establishes the requirements for the preparation of and the application to the electrode of the asbestos used in the fabrication of the O_2/N_2 prototype module (NAS 9-13720).

2. Applicable Documents

Lockheed	
LMSC-D401948	The Development of a Non-Cryogenic Nitrogen/ Oxygen Supply System

3. Requirements

3.1 Materials and Equipment

3.1.1 Materials. Materials used in this process are:

1. Grinder suitable for reducing sheet asbestos to pulp.
2. Fixture suitable for holding electrode while slurry is applied and water is removed.
3. Temperature controlled oven.

3.2 Process Procedure

3.2.1 Asbestos Preparation. The sheet asbestos shall be chopped into small pieces and ground, with an appropriate amount of distilled water, to a pulp-like consistency. Additional distilled water shall be added as necessary to facilitate pouring of the slurry.

3.3 Asbestos Application to the Electrolyte Spacer Membranes

3.3.1 Application. After the electrolyte spacer (with membranes attached) has been clamped into the appropriate fixture the exposed membrane shall be wetted with distilled or purified water. The slurry of asbestos and water shall then be poured onto the horizontal surface of the membrane and the fixture tilted back and forth to obtain an even distribution of the slurry. Excess water shall be allowed to drain through the membrane or alternatively shall be pulled through with a slight vacuum. The electrolyte spacer shall be "turned over" for a repeat of the process after sufficient water has been removed to allow adhesion of the asbestos to the membrane.

3.3.2 Drying. The asbestos shall be dried in an oven for not less than 4 hours at 35-46°C (95-115°F).

4. Quality Assurance Provisions

4.1 Test Methods

4.1.1 Materials Inspection. Materials inspection shall consist of verification that materials are in accordance with applicable specifications.

4.1.2 Visual Inspection. The dried asbestos shall be visually inspected for consistency of thickness, completeness of coverage and absence of holes.

5. Notes

5.1 Intended Use. This process specification is intended for use in asbestos preparation and slurrying as related to the O_2/N_2 prototype module (NAS 9-13720).

Appendix F

Process Specification

Annealing, Polysulfone

1. Scope. This specification establishes the requirements for the annealing of polysulfone parts used in the fabrication of the O_2/N_2 prototype module (NAS 9-13720).

2. Applicable Documents

Lockheed	
LMSC-D401948	The Development of a Non-Cryogenic Nitrogen/Oxygen Supply System

3. Requirements

3.1 Materials and Equipment

3.1.1 Materials. None.

3.1.2 Equipment. Controlled temperature oven of sufficient size and temperature range to accommodate part being annealed. Oven shall be capable of maintaining $3^{o}C(5^{o}F)$ or less temperature gradient across any 6 inch part span.

3.2 Process Procedure.

3.2.1 Part Preparation. Part shall be clean and dry. Caution: Do not clean part with volatile solvents.

3.2.2 Time and Temperature Cycle. The annealing cycle is a function of part thickness and shall be in accordance with LMSC-D401948.

4. Quality Assurance Provisions

4.1 Test Methods

4.1.1 Material Inspection. Material inspection shall consist of verification that materials are in accordance with applicable specifications.

4.1.2 Visual Inspection. The annealed part shall be visually inspected for distortion and dracking.

4.1.3 Test for Properly Annealed Part. The annealed part may be subjected to a 3 second dip in ethyl acetate or acetone. A properly annealed part will not stress crack.

Caution:- This constitutes destructive testing in the case of an improperly annealed part.

5. Notes

5.1 Intended Use. This process specification is intended for use in polysulfone annealing as related to the O_2/N_2 prototype module (NAS 9-13051).

Appendix G

Process Specification

Baseplate Bonding

1. Scope. This specification establishes the requirements for adhesive bonding of polysulfone baseplate parts used in the fabrication of the O_2/N_2 prototype module (NAS 9-13051).

2. Applicable Documents.

Lockheed

LMSC-D401948 The Development of a Non-Cryogenic Nitrogen/Oxygen Supply System

3. Requirements

3.1 Materials and Equipment

3.1.1 Materials. Materials used in this adhesive bonding method are as follows:

1. Shell Epon 828 2 part epoxy adhesive
2. Isopropyl alcohol
3. Two (2) 24 inch lengths of .010 dia wire or .010 x .020 ribbon (material optional)

3.1.2 Equipment

1. Hydraulic press. sufficiently large to apply 5 psi over the entire baseplate surface.
2. One 2 inch x 12 inch steel straight edge
3. Beam scales
4. Containers as required for weighing and mixing adhesive components.

3.2 Process Procedure

3.2.1 Surface Preparation. Surfaces to be bonded shall be lightly abraded with a suitable abrasive cloth or paper to remove surface gloss, followed by cleaning to remove residual abrasive particles with detergent and water.

3.3 Preparation and Adhesive. Resin and hardener shall be weighed and mixed in a ratio of 4 parts resin to one part hardener. Mixing shall be done in a manner which introduces as little air as possible to the mixture. Useable pot life at room temperature will be 15-20 minutes.

3.4 Application of Adhesive

3.4.1 Application. An even coating of adhesive approximately .01 in. thick shall be applied to the closure surface only. The faying surfaces of the closure and main body shall be immediately joined in a manner to preclude the introduction of air bubbles into the adhesive layers. The assembled parts shall be placed in a horizontal press and subjected to a pressure of 3-5 psi. The assembly shall remain in the press until cured. Adhesive squeeze out shall be removed by an appropriate method not involving volatile solvents.

3.4.2 Cure. The adhesive shall be cured for not less than 24 hours at room temperature.

4. Quality Assurance Provisions

4.1 Test Method

4.1.1 Materials Inspection. Materials inspection shall consist of verification that all materials are in accordance with applicable specifications.

4.1.2 Visual Inspection. The bonded baseplate shall be inspected visually for air inclusions in the bond line. Small inclusions are acceptable as long as they do not form a path between two adjacent passages.

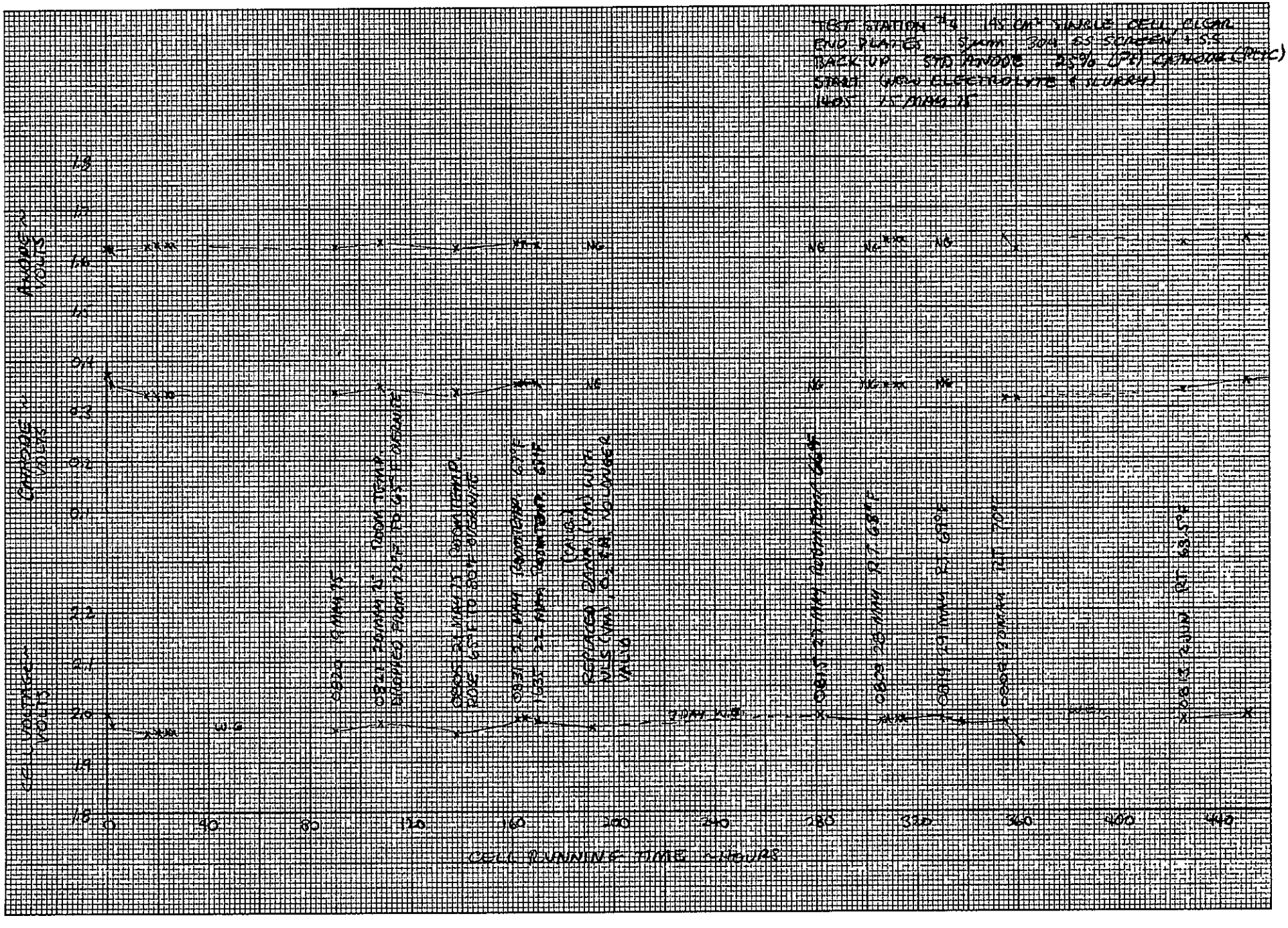
4.1.3 Pressure Testing. Pressure tests shall be conducted with both water and gaseous nitrogen to assure the pressure integrity of all internal passages. Test pressure shall be 37.5 psi.

5. Notes

5.1 Intended Use. This process specification is intended for use in baseplate bonding as related to the O_2/N_2 prototype module (NAS 9-13051).

APPENDIX H

LONG TERM SINGLE CELL TEST DATA



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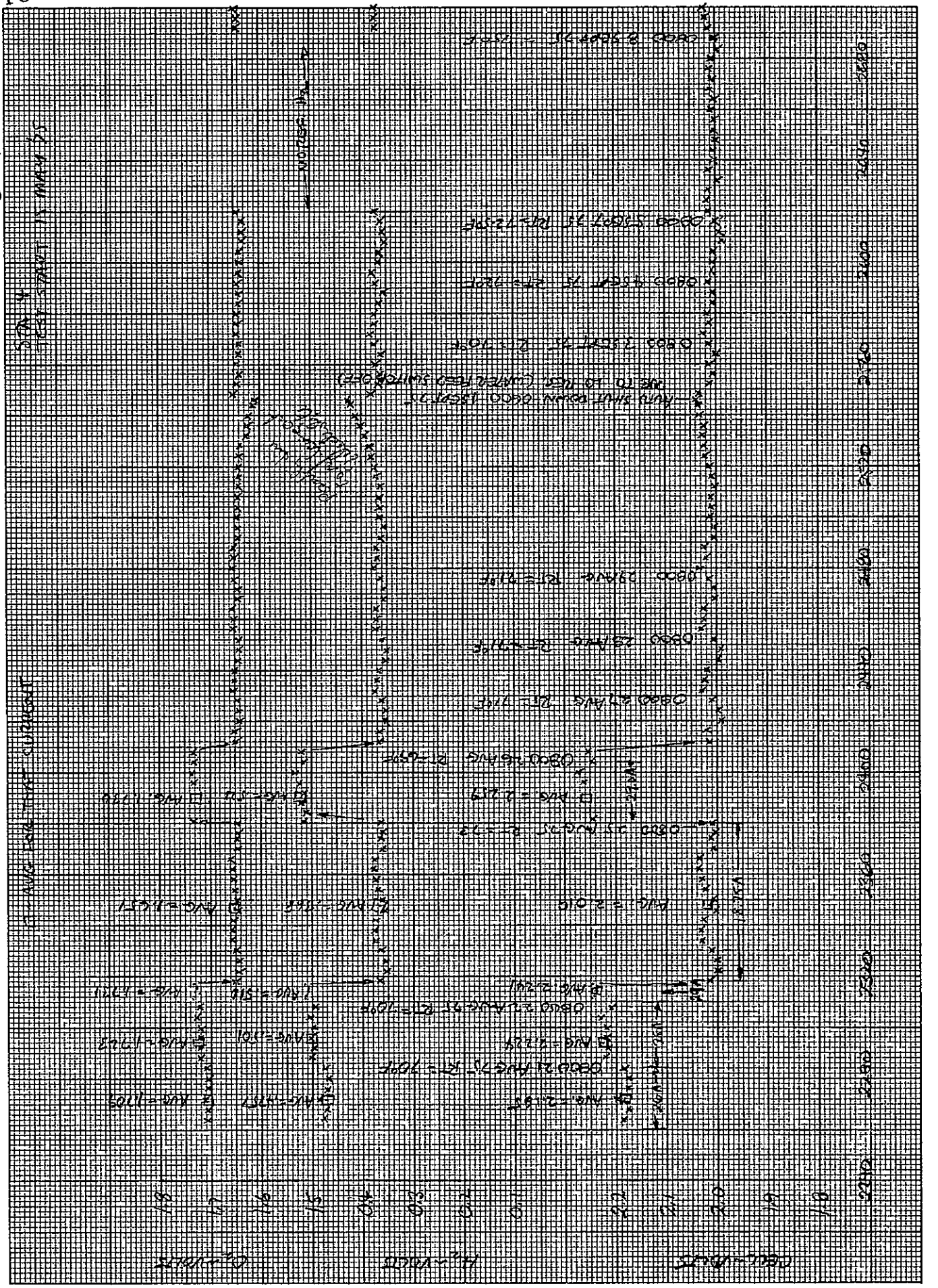

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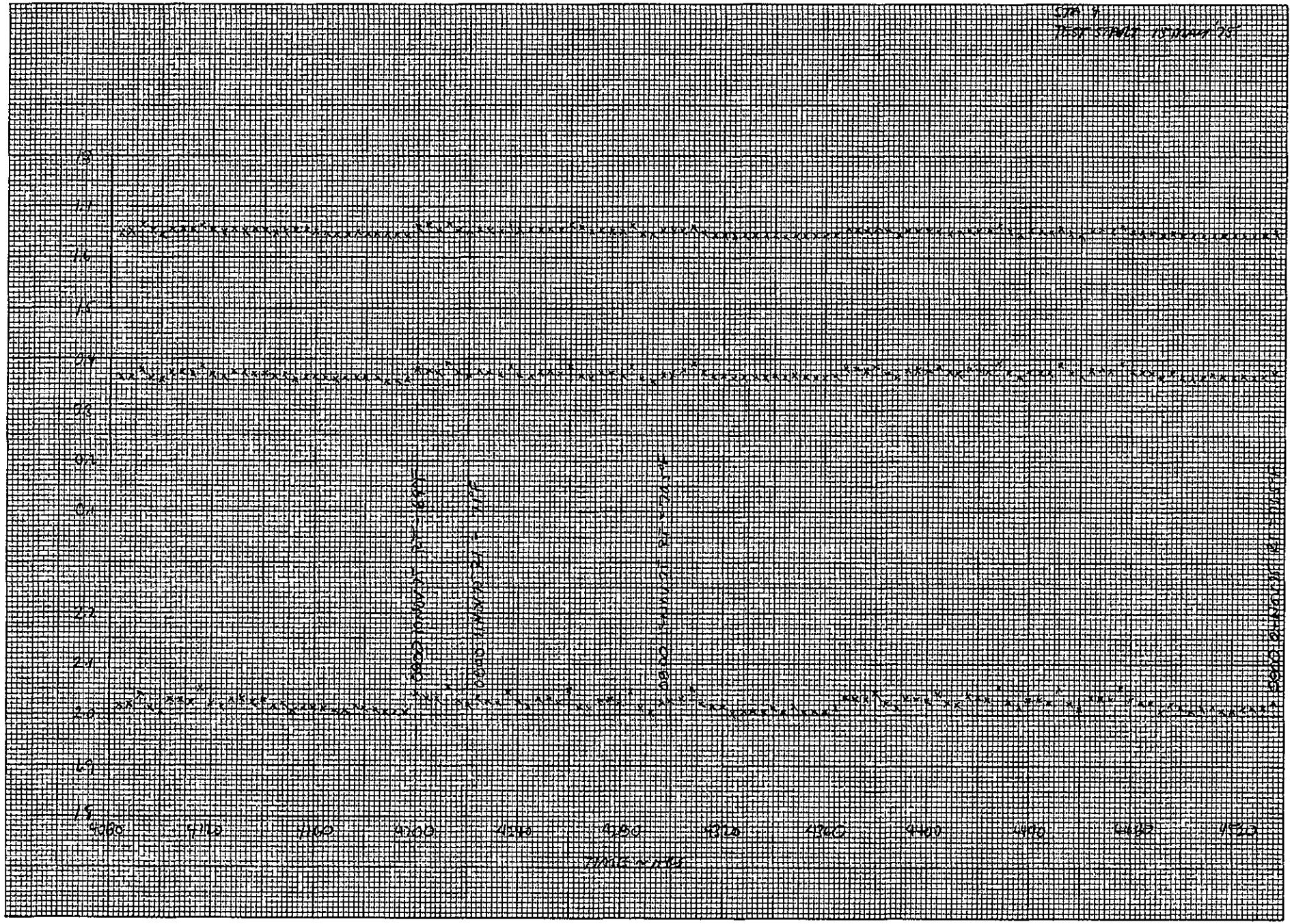

ADDENDUM TO CONTRACT

NAS 9-13720

THE TESTING OF A HYDROGEN CONCENTRATOR

NAS 9-13720 ADDENDUM

TABLE OF CONTENTS

NAS 9013720 ADDENDUM

LIST OF FIGURES

1.0 Introduction

Approximately $10K in supplemental funding was added to contract NAS 9-13720 for the purpose of investigating a technique for purifying gaseous nitrogen from a nitrogen generation stage. The generation unit was defined as one which produces a mixture of nitrogen and hydrogen and consequently a hydrogen concentrator was chosen for the investigation. One objective of the investigation was to determine if it was feasible to use a single cell from the O_2/N_2 module of NAS 9-13720.

2.0 Nitrogen Purification/Separation

2.1 Task Description

The purpose of this task was to conduct a primarily experimental investigation into a technique for separating nitrogen from hydrogen in the effluent of a nitrogen generator. A single cell from the existing, circulating electrolyte O_2/N_2 module was used as the separation unit. The single cell was chosen since it was felt that only minor modifications would be required to make it work as an H_2 concentrator.

The investigation was to cover a range of hydrogen concentrations representing three sources:

1) Low concentration hydrogen that would come from the anode side of an electro-chemical source operating in the hydrogen regime. This case represents the existing O_2/N_2 cell.
2) Medium concentration hydrogen that would come from the cathode side of the existing O_2/N_2 cell where it is available due to the inherent inefficiencies associated with the electrochemical breakdown of hydrazine.
3) High concentration hydrogen that would come from a generator which catalytically decomposes hydrazine.

Although potential integration problems between the generator and separator stages were to be considered, the testing was to be primarily concerned with the technical aspects of the separation stage. The testing was to define operating conditions, critical control aspects and material effects, while

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Although potential integration problems between the generator and separator stages were to be considered, the testing was to be primarily concerned with the technical aspects of the separation stage. The testing was to define operating conditions, critical control aspects and material effects, while

detail design and configuration efforts would be limited to that required to produce useful test results. The nitrogen purification goal was to obtain 99.9% nitrogen out of the separation stage. Test objectives were to have the following priorities:

1) Purification stage operating conditions and material requirements.
2) Specific component design and configuration features and requirements.
3) System integration and control concepts to the extent possible.

Prior to any testing, a test plan was to be submitted to the technical monitor for review and approval. This test plan was to be updated as necessary to best utilize the test results as they were obtained.

3.0 Technical Discussion

3.1 Planned Tests

The planned tests were divided into three categories:

1) Those tests necessary to set up and check out the test facility.
2) Tests required to verify the calculated values for consumed and generated hydrogen for various current densities.
3) Test required to verify the ability of the single cell to separate hydrogen and nitrogen effectively.

Category 1) and 2) tests were to be combined, with the main objective being the definition of current vs. hydrogen flow rate and then be used to set those values in the category 3) tests.

Current vs hydrogen consumption rate data is critical in setting the amount of hydrogen available at the electrode for a given current. If insufficient hydrogen is available, hydrogen starvation occurs and the voltage rises. If the voltage is allowed to rise above about one volt, oxygen production begins and a mixture of hydrogen and oxygen may be present in the system. This situation is to be avoided.

3.1.1 Test Set-up Description

The laboratory test station used for these tests was one which was previously used for single cell O_2/N_2 testing. Only minor modifications and additions were necessary to perform the required testing. Figure 1 presents a schematic of the test set up. For purposes of this testing, a hydrogen supply was needed only at the anode. However, a second hydrogen supply was provided for the cathode side and was used as the purge medium prior to the application of power. This insured that the cathode was never exposed to any gas other than hydrogen and therefore gas analysis was required only to establish the amount of water vapor in the input gasses; also as a check on the output gases. Flow rate and pressure were measured and recorded for the two input gases prior to mixing and introduction at the anode. Metering valves were installed ahead of the flowmeter in each gas line for adjusting the mixture ratio. If only hydrogen or nitrogen was desired, the opposite valve could be closed. Pressure gages were installed downstream of the input flow meters so that the input and output flow rates could be normalized. Output flows were to ambient pressure. The remaining equipment included an adjustable power supply, an ammeter, a voltmeter, an electrolyte pump, an electrolyte reservoir and a heat exchanger. The cooling capacity of the heat exchanger was never required. Septums for gas sampling were provided on each of the outlet lines and on the gas mixture inlet line. The anode and cathode were alike, both being the O_2/N_2 anode configuration.

One modification was made to the single cell. The anode gas spacer was partitioned with rubber bumpers (used as spacers in the O_2/N_2 cell) to provide a flow path approximately 72 cm (28.5 in.) long.

3.2 Tests Performed

The first test used hydrogen only. Its purpose was to establish the voltage, current profile for currents up to ten amps. In order to insure that there would be excess hydrogen flow over the anode, a hydrogen consumed vs. current curve was calculated (Figure 2). This curve predicted that about

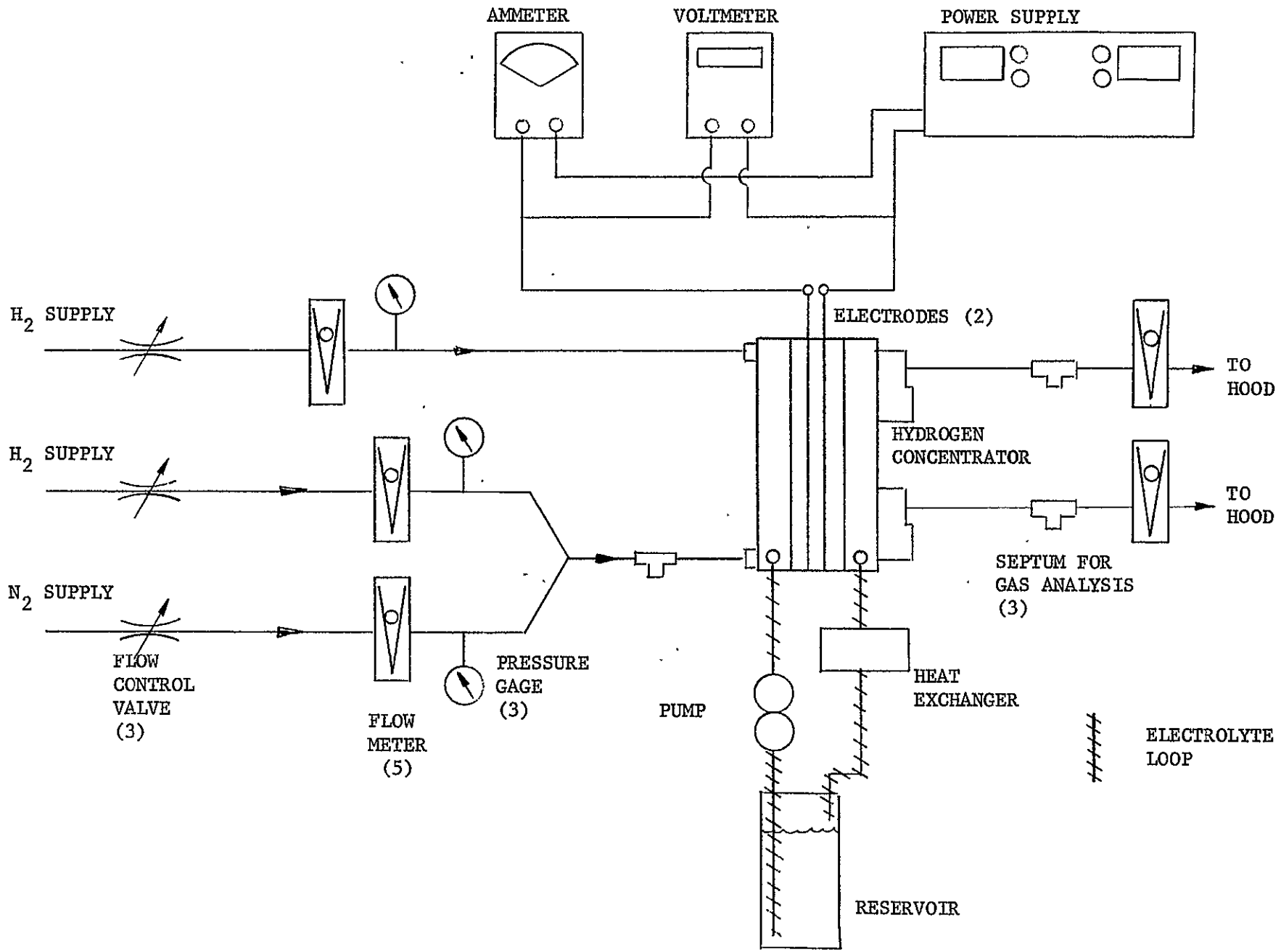

Figure 1 Hydrogen Concentrator Test Set Up Schematic.

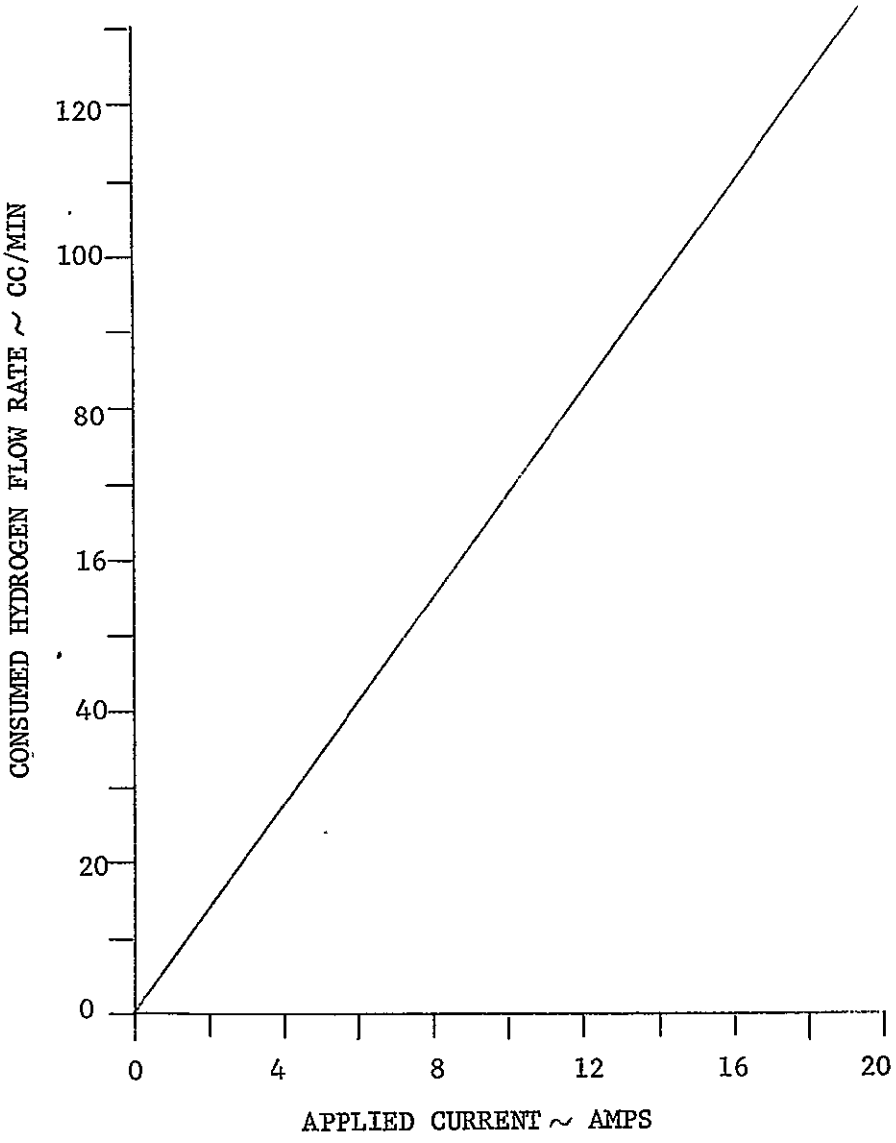

Figure 2 Theoretical Hydrogen Consumed for Various Voltages

70 cc/min of hydrogen would be consumed at 10 amps. A "pad" of about 10% was added and the hydrogen flow rate was set at about 30 cc/min. The hydrogen was allowed to purge the system for about 15 minutes and then power was applied and the test begun. The current was raised to 10 amps in 2 amp steps, then lowered to 0 amps in 2 amp steps. The resulting voltage/current profile is shown in Figure 3. The maximum total voltage recorded at 10 amps was 0.31 volts. This is somewhat more than the sum of the anode (0.16 volts) and cathode (0.12 volts) voltages. This discrepancy is due to the fact that no digital voltmeter was available and a conventional voltmeter was used. Its reading accuracy was only fair. This current/voltage profile indicated that there was no danger of getting into the oxygen regime if current was limited to 10 amps or less and if an excess of hydrogen (per Figure 2) was available to the anode. Later runs were made using currents greater than 10 amps but only after additional operating experience had been gained.

The second series of runs served several purposes:

1) They provided the learning curve for setting the hydrogen/nitrogen mixture ratios.
2) They pointed up the necessity of determining the amount of water vapor in the mixture and of normalizing the consumed and generated flow rates.
3) They established input flow rates that could be reasonably measured with the limitations of the available flow meters.
4) They provided a preview of the difficulties to be encountered in trying to run medium and low hydrogen/nitrogen ratios.
5) They established the operating procedures required to insure excess hydrogen relative to the current being used.

The third series of tests was to have run high, medium and low hydrogen/nitrogen ratios but only the high ratio runs were completed. The problems encountered are discussed in the next section.

3.3 Test Results

3.3.1 Control Aspects

During the running of the second series of tests it was noted that a voltage continued to exist across the cell after the current was turned off. This

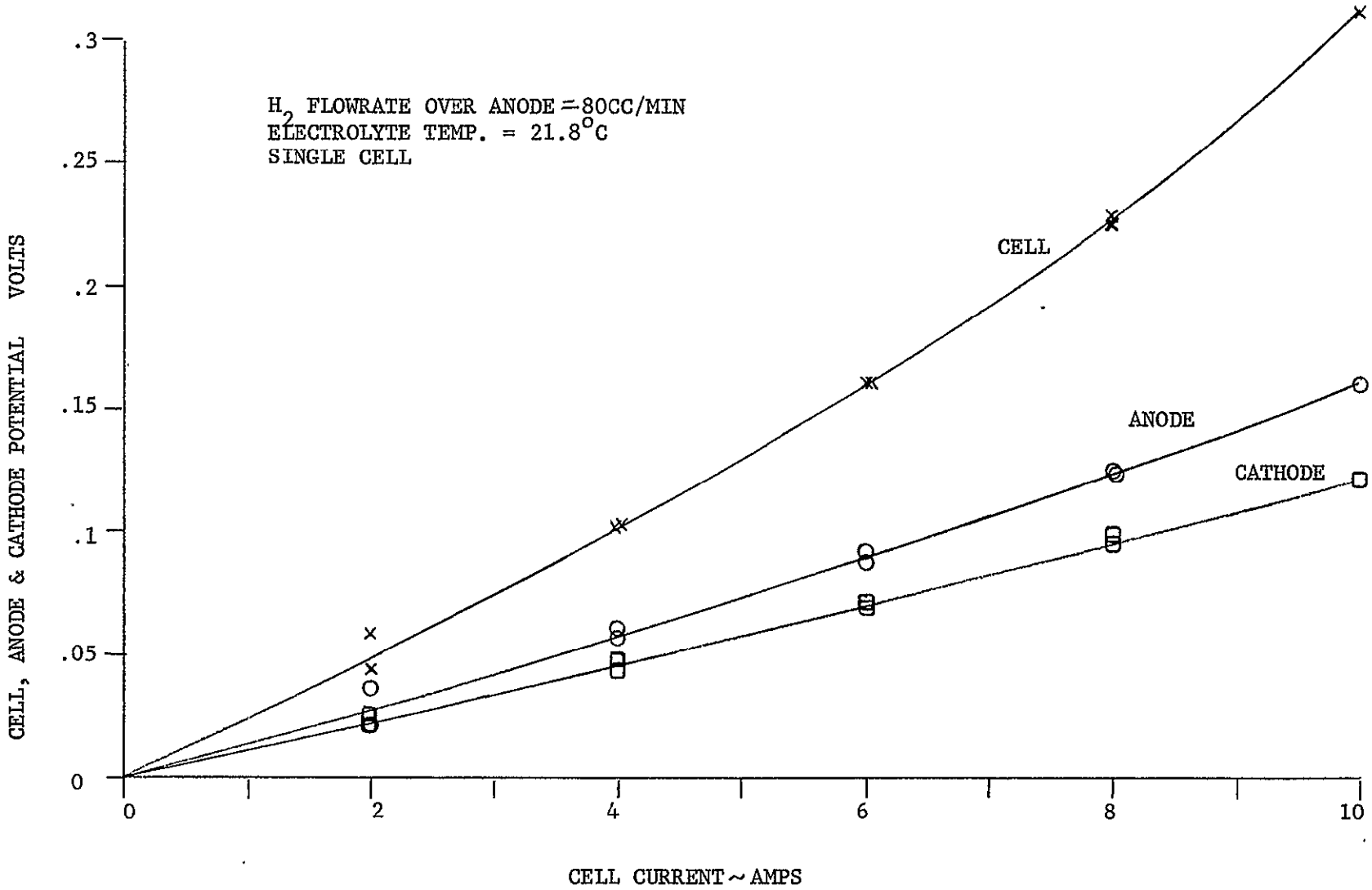

Figure 3 Hydrogen Concentrator Current Profile

occurred at the end of the day, so the cell was allowed to stand overnight, with no power, to see if the charge would bleed off. It did not and the cell had to be shorted to get zero volts for zero current. More runs were made in an attempt to repeat the original voltage/current profile (using pure hydrogen). These runs produced voltage in excess of 1.0 volts at about 12 amps. Each time a run was terminated the cell had to be shorted back to zero volts. It was finally decided that the anode had been damaged due to hydrogen starvation. Further, it was concluded that the hydrogen starvation was caused by the inadvertant reduction of hydrogen flow before current was reduced. To verify this idea, a run was made which started with an excess of hydrogen (only) for a given current. The current was held steady and the hydrogen flow slowly reduced. The electrolyte temperature and voltage were observed as the hydrogen flow was reduced. As the hydrogen flow rate decreased through the point where the supply rate equaled the consumption rate, the voltage started to rise as did the electrolyte temperature. The hydrogen flow was reduced until a voltage of about 1.2 volts was achieved and then the current was reduced to zero. As expected, the voltage did not drop. It was therefore decided to disassemble the cell and replace both electrodes. It is uncertain how hydrogen starvation effects electrode performance; there was no visable damage to the electrode. The cell was reassembled using two "new" electrodes from the prototype module cell stack. It then performed satisfactorily as long as an excess of supply hydrogen was provided.

The above events provided considerable insight into the operation of this hydrogen concentrator. First, it is essential that all points on the electrode be supplied with hydrogen at a rate of at least equal to the predicted consumption rate. Even though only a small area may be starved (due to uneven flow) the system reacts as though the whole electrode is starved. In this concentrator, an excess of hydrogen is required. The presence of excess hydrogen means that the goal of 99.9% nitrogen out could not be achieved, at least not in one pass through the separator. The achievement of 99.9% nitrogen may lie in precise current control in conjunction with a very

homogeneous electrode and turbulant flow, evenly distributed over the surface of the electrode. A supply gas mixer (upstream of the unit) would probably be desirable as well. The current would be continuously adjusted upward until the onset of starvation was indicated by a slight increase in voltage. The current would then be stepped down in predetermined increments until the voltage rise stopped and/or reversed. The cycle would then be repeated.

3.3.2 Mixture Flow Pattern

These tests also indicate that the manner in which the gas mixture is presented at the electrode has some effect on the amount of hydrogen that is consumed, i.e. if all the available hydrogen is to be consumed, it must be presented at the surface of the electrode. Further, there seems to be some "residence time" requirement, this because lower flow rates produced consumed hydrogen values closer to the calculated values than did higher flow rates. While the relatively long narrow flow path of the test cell provided a relatively long residence time, it is doubtful that much turbulance was present in the gas stream. A more optimum method might be to introduce the gas stream perpendicular instead of parallel to the plane of and at the center of the electrode. The gas would then flow in all directions across the face of the electrode. Turbulance generators would be placed radially about the inlet nozzle. The output gas would be collected all around the edge of the electrode This approach suggests a circular electrode.

3.3.3 High, Medium and Low Concentration Runs

High concentration hydrogen was selected for the first run since previous experience said it had the highest probability of success (and there was little budget left).

The initial run used a gas mixture of 70% hydrogen and 30% nitrogen and a total flow rate of 150 cc/min. The resulting hydrogen input rate was 99.7 cc/min and the nitrogen rate was 43.1 cc/min. With the current set at 10 amps, an excess hydrogen flow rate of 30 cc/min was provided. The total input flow rate was 142.8 cc/min while the effluent flow rate was 69.9 cc/min.

43.1 cc/min was nitrogen, leaving 26.8 cc/min as unconsumed hydrogen. The apparent 3 cc/min discrepancy may be attributed to inaccuracies in flow and current measurement, e.g. if the current was actually 10.4 amps, the anode input and output were balanced. The predicted consumption rate for 10.4 amps is 72.2 cc/min. The hydrogen consumed (73 cc/min) was balanced (within measurement accuracy) with the 73.9 cc/min generated hydrogen.

The above example was typical of the six runs made, that is until the hydrogen portion of the input dropped below 25%. With hydrogen concentration below 25% (considered a medium concentration) the required nitrogen flow rate (typically 200-250 cc/min) exceeded the measurement capabilities of the available flowmeter and so the testing was terminated. It is felt that had more sophisticated measurement equipment been available, all of the testing might have been completed.

4.0 Conclusions

The testing discussed above shows that using an O_2/N_2 type of cell for the separation of nitrogen and hydrogen is quite feasible.

In order to realize the full potential of the separator, further development is necessary in the areas of current control, input flow distribution and electrode configuration.